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PHYSICOCHEMICAL CHARACTERIZATION OF HIGH-PERFORMANCE FIBRE-REINFORCED ORGANIC-MATRIX COMPOSITES

PART 2. APPLICATIONS OF INFRARED SPECTROSCOPY

by

K. C. Cole and D. Noël

Industrial Materials Research Institute
National Research Council Canada
75, boul. de Mortagne
Boucherville, Québec, Canada
J4B 6Y4

CANADA INSTITUTE FOR S.T.I.
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TABLE OF CONTENTS

List of figures....iii
List of tables....v
Preface....vi
Acknowledgement....vii
Summary....viii
Résumé....ix

1. INTRODUCTION....1

2. EXPERIMENTAL....3

2.1 Materials....3
2.2 Instrumentation....5
2.3 Heatable IR Cell Procedure....5

3. THE TRANSMISSION METHOD....8

3.1 Description of the Method....8
3.2 Choice of a Solvent....9
3.3 The Infrared Spectrum of Narmco 5208 Resin....10
3.4 Quantitative Analysis....20
3.5 Comparison of Different Batches....29
3.6 Resin Cure....30
3.7 Near-Infrared Spectroscopy....39
3.8 Recommended Procedure for Quantitative Analysis of Narmco 5208 Prepreg by IR Transmission....42

4. THE INTERNAL REFLECTION METHOD....44

4.1 Description of the Method....44
4.2 The ATR Spectrum of Narmco 5208 Prepreg....46
4.3 Quantitative Analysis by ATR....49
4.4 Comparison of Different Batches....55
4.5 Recommended Procedure for Quantitative Analysis of Narmco 5208 Prepreg by IR Spectroscopy Using ATR....56

5. THE DIFFUSE REFLECTION METHOD....58

5.1 Description of the Method....58
5.2 The Diffuse Reflectance Spectrum of Narmco 5208 Prepreg....61
5.3 Importance of Fibre Orientation....64
5.4 Quantitative Analysis by Diffuse Reflection....69
5.5 Prepreg Cure....75
5.6 Microanalysis by Diffuse Reflection....76
5.7 Recommended Procedure for Measuring IR Spectra of Composites by Diffuse Reflection....84

6. CONCLUSIONS....86

BIBLIOGRAPHY....88

LIST OF FIGURES

Figure	Description	Page
1	Chemical structures of principal components of Narmco 5208 resin	4
2	Diagram of heatable IR transmission cell used to study epoxy cure	6
3	Transmission IR spectrum of Narmco 5208 resin Batch 1010 (uncured) in transmittance units	12
4	Transmission IR spectrum of Narmco 5208 resin Batch 1010 (uncured) in absorbance units	13
5	Transmission IR spectrum of Ciba-Geigy Araldite MY 720	14
6	Transmission IR spectrum of Ciba-Geigy Hardener HT 976	15
7	Transmission IR spectrum of Celanese Epi-Rez SU-8	16
8	Absorption bands used for quantitative analysis of Narmco 5208 resin	17
9	Transmission IR spectrum of Narmco 5208 resin Batch 1010 (cured)	19
10	Effect of sample thickness variation on measured absorbance	24
11	Transmission IR spectra of Narmco 5208 resin: Specimen #1 - film of uniform thickness; Specimen #4 - film of varying thickness	25
12	Relationship between peak absorbance values for spectra of Figure 11	26
13	Temperature program used for IR study of Narmco 5208 cure	31
14	Evolution of IR transmission spectrum during cure of Narmco 5208	33
15	Variation of "single sulphone" index as measured by IR transmission during cure of Narmco 5208 resin	34
16	Variation of "multiple sulphone" index as measured by IR transmission during cure of Narmco 5208 resin	35
17	Variation of "single epoxy" index as measured by IR transmission during cure of Narmco 5208 resin	36
18	Variation of "multiple epoxy" index as measured by IR transmission during cure of Narmco 5208 resin	37
19	Variation of "epoxy + aromatic" index as measured by IR transmission during cure of Narmco 5208 resin	38
20	Near-infrared transmission spectra of Narmco 5208 resin	41
21	Attenuated total reflectance IR spectrum of Narmco 5208/WC3000 prepreg Batch 1010 recorded using 45° KRS-5 prism	47

22	Attenuated total reflectance IR spectrum of woven graphite cloth recorded using 45° KRS-5 prism	48
23	ATR spectrum of Narmco 5208/WC3000 prepreg after baseline correction and normalization	50
24	Comparison of transmission and normalized ATR spectra of Narmco 5208	51
25	Diffuse reflectance IR spectrum of Narmco 5208/WC3000 prepreg Batch 1010, as recorded	62
26	Diffuse reflectance IR spectrum of woven graphite cloth	63
27	Diffuse reflectance IR spectrum of Narmco 5208/WC3000 prepreg after conversion to Kubelka-Munk units and baseline correction	65
28	Diffuse reflectance IR spectrum of Narmco 5208/WC3000 cured laminate, as recorded	66
29	Diffuse reflectance IR spectrum of Narmco 5208/WC3000 cured laminate, after conversion to Kubelka-Munk units and baseline correction	67
30	Effect of fibre orientation on diffuse reflectance IR spectrum of Narmco 5208/WC3000 prepreg and cured laminate	68
31	Comparison of transmission, specular reflectance, and diffuse reflectance spectra of Narmco 5208 resin and prepreg	71
32	Effect of covering with KBr on the diffuse reflectance IR spectrum of Narmco 5208/WC3000 prepreg	73
33	Effect of embedded KBr on the diffuse reflectance IR spectrum of Narmco 5208/WC3000 prepreg	74
34	Evolution of diffuse reflectance IR spectrum during cure of Narmco 5208/WC3000 prepreg	77
35	Variation of "single sulphone" index as measured by diffuse reflectance IR during cure of Narmco 5208/WC3000 prepreg	78
36	Variation of "multiple sulphone" index as measured by diffuse reflectance IR during cure of Narmco 5208/WC3000 prepreg	79
37	Variation of "single epoxy" index as measured by diffuse reflectance IR during cure of Narmco 5208/WC3000 prepreg	80
38	Variation of "multiple epoxy" index as measured by diffuse reflectance IR during cure of Narmco 5208/WC3000 prepreg	81
39	Diffuse reflectance IR spectrum of pure TGDDM monomer obtained by liquid chromatographic separation of MY 720	82
40	Diffuse reflectance IR spectrum of 1 μg of Narmco 5208 resin	83

LIST OF TABLES

Table	Description	Page
1	Narmco 5208 IR spectrum band assignments	11
2	Quantitative analysis of Narmco 5208/WC3000 prepreg Batch 1010 by IR transmission (first experiment)	21
3	Quantitative analysis of Narmco 5208/WC3000 prepreg Batch 1010 by IR transmission (second experiment)	27
4	Quantitative analysis of Narmco 5208/WC3000 prepreg Batch 1014 by IR transmission	28
5	Quantitative analysis of different batches of Narmco 5208 by IR transmission	29
6	Quantitative analysis of Narmco 5208/WC3000 prepreg Batch 1010 by attenuated total reflection IR	53
7	Comparison of IR transmission and ATR results for Narmco 5208/WC3000 prepreg Batch 1010	54
8	Quantitative analysis of different batches of Narmco 5208/WC3000 prepreg by attenuated total reflection IR	55
9	Quantitative analysis of Narmco 5208/WC3000 prepreg Batch 1010 by diffuse reflection IR	70
10	Quantitative analysis of Narmco 5208/WC3000 prepreg Batch 1014 by diffuse reflection IR	75

PREFACE

This report is the second of a series resulting from a cooperative effort involving the Industrial Materials Research Institute (IMRI) of the National Research Council Canada (NRCC) (Boucherville, Québec) and Canadair Limited (Montréal, Québec). The subject is one of growing importance in high-technology manufacturing, namely the physicochemical characterization of high-performance fibre-reinforced organic-matrix composites. The first report in the series contains a general discussion of the subject followed by a review of the recent literature. Subsequent reports describe the results of original research involving the application of various chromatographic and spectroscopic techniques to typical commercial composite systems, with particular attention given to the graphite-epoxy system Narmco Rigidite 5208/WC3000. This particular report deals with infrared spectroscopy. The titles of the complete series are as follows:

Part 1. General Discussion and Literature Review
Part 2. Applications of Infrared Spectroscopy
Part 3. Applications of Liquid Chromatography
Part 4. Applications of Pyrolysis Gas Chromatography and Thermal Analysis
Part 5. A Study of the Room-Temperature Aging of Narmco 5208/WC3000 Prepreg
Part 6. Methods for Quality Control of Matrix Chemistry

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SUMMARY

The report describes a systematic investigation of the application of infrared spectroscopy to the analysis of fibre-reinforced organic-matrix composites, using as a test case the graphite-epoxy system Rigidite 5208/WC3000 manufactured by Narmco Materials, Inc. Three methods of obtaining the IR spectrum (transmission, internal reflection, and diffuse reflection) have been studied and compared, and the advantages and disadvantages of each are discussed. Although it appears to be a widely accepted method for quantitative analysis of uncured resin, the transmission method is shown to be subject to considerable error due to nonuniform thickness of cast films. Very careful sample preparation is needed to give acceptable results. The internal reflection method is better for quantitative analysis because it gives more reproducible results and can be applied directly to prepreg. This avoids the problem of nonuniform thickness and also results in considerable time savings in sample preparation. The diffuse reflection method is not recommended for quantitative work with composites because it is subject to variations due to front-surface (Fresnel) reflection and scattering effects. However, it is an excellent method for qualitative work because it allows measurement of both uncured and cured samples with practically no sample preparation. It could be used as a nondestructive method for confirming completion of cure in finished parts. It is also a quite sensitive method for analysing small quantities of material such as fractions of samples separated by liquid chromatography. Although most IR work is done in the mid-infrared region (4000 - 400 cm^{-1}), the near-infrared region is also interesting for the study of Narmco 5208 since it provides information on the degree of cure and the moisture content.

RÉSUMÉ

Le rapport a pour sujet l'application de la spectroscopie infrarouge à l'analyse des composites à base de renforts fibreux et matrices organiques. Les différentes méthodes d'analyse ont été développées en utilisant le système graphite-époxyde Rigidite 5208/WC3000 fabriqué par Narmco Materials Inc. Trois méthodes pour obtenir le spectre infrarouge (transmission, réflexion interne, réflexion diffuse) ont été étudiées et comparées pour souligner leurs avantages et leurs inconvénients respectifs. Bien qu'elle soit couramment utilisée pour l'analyse de la résine non-durcie, la méthode de transmission est sujette à des erreurs importantes résultant de la non-uniformité de l'épaisseur du film déposé sur la fenêtre. Pour obtenir des résultats fiables, une préparation très soignée de l'échantillon est nécessaire. La méthode de réflexion interne est meilleure pour l'analyse quantitative parce qu'elle fournit des résultats plus reproductibles. De plus, le préimprégné peut être analysé sans extraction de la résine avec un solvant. Ainsi, cette méthode évite le problème d'épaisseur non-uniforme et permet des économies importantes en temps de préparation. La méthode de réflexion diffuse n'est pas recommandée pour l'analyse quantitative des composites parce que les spectres sont influencés par la réflexion Fresnel et par la diffusion du rayonnement infrarouge. Néanmoins, il s'agit d'une excellente méthode pour les mesures qualitatives puisqu'elle permet de mesurer les échantillons durcis et non-durcis avec très peu de préparation. Elle pourrait être utile comme méthode non-destructive pour confirmer l'achèvement du durcissement dans les pièces finies. C'est aussi une méthode très sensible pour l'analyse de petites quantités de produit telles les fractions séparées par la chromatographie liquide. Bien que la plupart des mesures dans l'infrarouge soient effectuées dans l'infrarouge moyen (4000 - 400 cm^{-1}), le proche infrarouge s'avère également intéressant pour l'étude du Narmco 5208, puisqu'il fournit des informations concernant le degré de durcissement et le taux d'humidité.

1. INTRODUCTION

This report is part of a series concerned with the application of physicochemical testing methods to high-performance composite materials consisting of high-strength reinforcing fibres (glass, carbon, graphite, Kevlar®) embedded in an organic polymer matrix (epoxy, polyimide, or polyester). As outlined in the first report [1], the objective of the research project was to develop improved methods for the rapid and accurate characterization of the chemical composition of the organic matrix materials. Such methods are being used more and more for quality control as composite materials are increasingly used in ever more critical applications, particularly in the aerospace industry. The first report also gives a general discussion of the subject and a comprehensive review of the recent literature including some 300 references.

This particular report is concerned with one particular technique, namely infrared spectroscopy. This technique [2-6] has a long tradition as one of the most extensively used for characterizing a wide range of materials, including composites [7-9]. When matter is exposed to infrared radiation it usually absorbs energy at specific frequencies which correspond to the characteristic frequencies of vibration of the atomic groups making up the material. A graph of the degree of absorption versus frequency is known as the infrared spectrum. Often it is quite detailed and serves as a unique "fingerprint" of the material, so IR spectroscopy is widely used for identifying unknown samples. In addition, since the absorption is directly related to the amount of material, it can be used as a quantitative analysis method. It is also used to study changes in molecular structure which occur as a result of chemical reaction. It can be applied to solids, liquids, and gases. In the case of composite matrices, it is used in a number of ways, for example: qualitative and quantitative analysis of the resin, study of the curing reaction, and study of environmental degradation. Several examples are cited in the literature review previously mentioned [1].

The last ten years have seen a tremendous growth in the use of Fourier transform infrared (FTIR) spectrometers [5,6]. These instruments, which make use of interferometers rather than monochromators to analyse the frequency distribution of the radiation, are extremely powerful. Compared to conventional instruments they are much more sensitive, rapid, and precise, and their use of computers makes it possible to extract much more information from the spectrum. The high sensitivity makes it possible to successfully use a number of reflectance methods, thereby extending the range of applications to a greater number of materials. The possibilities of this technique have only just begun to be exploited.

This report describes the results of research performed with the aim of better understanding the factors which influence the infrared spectra of composite materials, in order to develop more fully its potential. Three different methods of obtaining the spectrum were investigated: transmission, attenuated total reflection, and diffuse reflection. The advantages and disadvantages of all three are compared for both qualitative and quantitative analysis. Most of the results described herein were obtained for one particular composite system, Rigidite 5208/WC3000 from Narmco Materials, Inc. Applications of the method to other systems will be described in a subsequent report (Part 6 of this series).

2. EXPERIMENTAL

2.1 Materials

The composite system chosen for intensive study was the Rigidite 5208/WC3000 system sold by Narmco Materials, Inc. The reinforcement consists of Celion graphite fibres, 3000 fibres per yarn, woven in an 8-harness satin pattern (each warp yarn passing alternately over seven fill yarns and under one fill yarn). The woven fabric is impregnated with Narmco 5208 resin to a nominal resin content of 42% by weight and the prepreg is supplied on a plastic backing sheet in rolls. The recommended cure schedule consists of a one-hour dwell at 135°C (275°F) followed by a two-hour cure at 177°C (350°F).

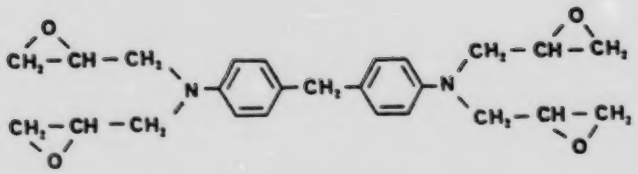
It has been reported [10-14] that Narmco 5208 consists primarily of three components. The major epoxy, which accounts for about 70% by weight, is based on TGDDM (tetraglycidyldiaminodiphenylmethane). A common commercial product of this type is Ciba-Geigy Araldite MY 720. The second most important component (about 22% by weight) is the curing agent DDS (diaminodiphenylsulphone); an example of a commercial grade of this material is Ciba-Geigy Hardener HT 976. There is also a minor epoxy (about 8% by weight) which is of the bisphenol A Novolac type (for example, Celanese Epi-Rez SU-8). The chemical structures of these are given in Figure 1. The DDS is a relatively pure material, but the epoxy resins consist of a mixture of monomer, oligomers, and other products (starting materials and by-products). A more detailed discussion of the Narmco 5208 system, including composition, analysis, and the nature of the curing reaction, is given in an earlier report [1].

The following samples of the Narmco 5208 system were supplied by Canadair Ltd.:

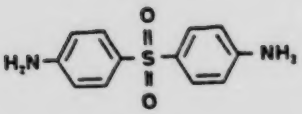
Prepreg, Batch Number 1010
Prepreg, Batch Number 1014
Prepreg, Batch Number 1101
Prepreg, Batch Number 1103
Prepreg, Batch Number 1104
Neat resin on plastic backing sheet, Batch Number 1047
Neat resin in bulk form, Batch Number 1023.

Prepreg and reactive resin samples were stored in a freezer at all times except for sampling and performance of experiments. Samples of the following components were obtained from the respective companies:

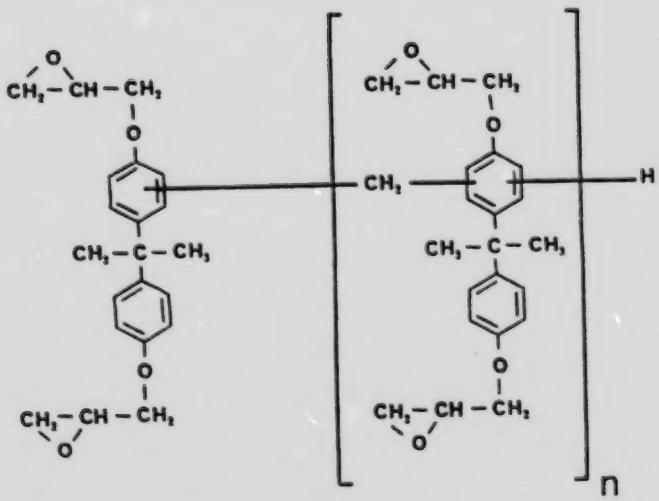
Ciba-Geigy Araldite MY 720 epoxy resin (TGDDM), Lot Y5085
Ciba-Geigy Hardener HT 976 (DDS), Lot IL 2096
Celanese Epi-Rez SU-8 (bisphenol A Novolac epoxy), Lot L11-82182.



TGDDM



DDS



Bisphenol A Novolac Epoxy

Figure 1 - Chemical structures of principal components of Narmco 5208 resin.

These were stored in a refrigerator.

2.2 Instrumentation

Infrared spectra were recorded using a Nicolet Instruments Model 170SX Fourier transform infrared spectrometer equipped with a wide-range liquid-nitrogen-cooled mercury cadmium telluride detector. The following accessories from Harrick Scientific Corporation were also used:

(1) Twin Parallel Mirror Reflection Attachment (Variable Angle Manual) with Internal Reflection Accessory using single-pass parallelogram prisms (50 x 10 x 3 mm); for attenuated total reflectance measurements.

(2) Diffuse Reflection Attachment (Praying Mantis Model); for diffuse reflectance measurements.

(3) External Specular Reflection Attachment with angle of incidence 30°; for specular reflectance measurements.

(4) Temperature-Controlled Cell TFC-M25 with Automatic Temperature Controller ATC-10G.

Most infrared spectra were recorded using an accumulation of 128 scans with a resolution of 4 cm^{-1} and Happ-Genzel apodization. Further details are given in subsequent sections in the discussion of results.

2.3 Heatable IR Cell Procedure

The experimental setup used to study resin cure by IR transmission is shown in Figure 2. It includes a Model TFC-M25 heatable cell with two heating elements, manufactured by Harrick Scientific Corporation. Two potassium bromide disks of diameter 13 mm and thickness about 0.8 mm are made by pressing KBr powder in a typical KBr pellet die. Their spectra are recorded and epoxy resin is deposited from acetone solution on one of the disks to give a film of suitable thickness. A "sandwich" is then formed using the other disk and placed between two specially-made aluminium

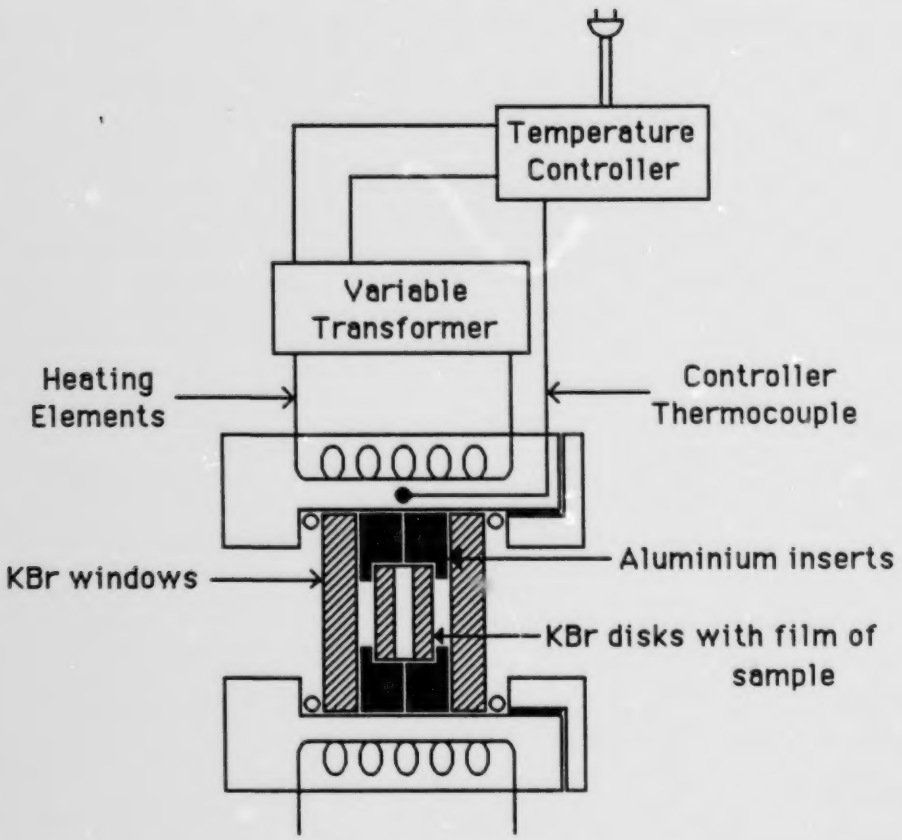


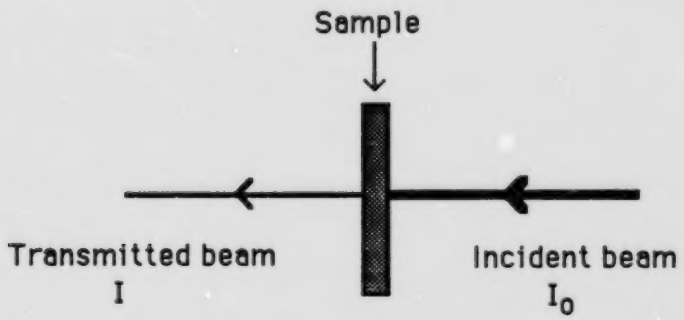
Figure 2. Diagram of heatable IR transmission cell used to study epoxy cure.

inserts. These in turn are placed between two outer KBr windows (25 x 2 mm) to reduce heat losses. The desired sample temperature is determined by a proportional controller (Harrick Model ATC-10G) connected to an iron-constantan thermocouple embedded in the body of the cell. The time taken to achieve this temperature can be controlled to some extent by a variable transformer connected between the controller and the heating elements. Because of heat losses there is a temperature differential between the controller thermocouple and the centre of the sample. It is difficult to monitor the true sample temperature during spectral measurement because a thermocouple placed at the centre of the sample would interfere with the IR beam. Hence a "calibration" was performed without recording spectra by passing a second thermocouple through a small hole drilled in one of the outer windows and placing it in contact with the centre of the sample. Using the calibration curves, the controller and transformer settings can be chosen to give the desired sample temperature profile.

3. THE TRANSMISSION METHOD

3.1 Description of the Method

This is the traditional, most widely used method of measuring infrared spectra, particularly for quantitative analysis. An IR beam is allowed to pass through the sample and the intensity I of the transmitted radiation is divided by that of the incident radiation I_0 to obtain the transmittance T, which is a function of the frequency. The graph of T versus frequency is the IR spectrum. Frequency is usually expressed in terms of the wavenumber, or the reciprocal of the wavelength, with units of cm^{-1}.



Often the sample consists of a solution contained between two transmitting windows. The Beer-Lambert law states that:

$$A = -\log_{10}T = abc$$

where A is known as the absorbance, a is the absorptivity (an intrinsic property of the absorbing species), b is the sample path length, and c is the concentration of the absorbing species. This equation makes it possible to perform quantitative analysis by using a cell of known path length and calibrating with solutions of known concentration. It has been used, for example, to analyse DDS in epoxy formulations using as solvents chloroform [10], dichloromethane [15], and acetonitrile [11,16]. Epoxy content has also been analysed in this way [10].

The solution method suffers from one important drawback. Most organic solvents absorb very strongly in the infrared region and will interfere with the absorption bands of

the material to be analysed. The few solvents which transmit well in the IR, such as chloroform, carbon tetrachloride, dichloromethane, and carbon disulphide, are often toxic, unpleasant, or will not dissolve the compound to be analysed. In the case of epoxy formulations, it becomes increasingly difficult to find a good solvent as the resin becomes more polymerized. Hence the solution method is of limited usefulness.

In this work, the solution method was rejected in favour of the cast film technique. The resin is dissolved in a suitable solvent, a few drops are placed on an IR-transparent window, and the solvent is evaporated. This leaves a thin film of resin which is measured in transmission. This method is simpler and faster than the solution method, but has one disadvantage. Usually it is difficult to determine the thickness of the film, so the amount of sample absorbing is unknown. This problem is overcome by using one peak in the spectrum as an "internal standard" or reference to which other peaks are compared. Other complications involved in this method are discussed later.

3.2 Choice of a Solvent

The following solvents were tested as candidates for extraction of Narmco 5208 resin from prepreg and casting of films for IR spectroscopy: tetrahydrofuran, acetone, acetonitrile, dichloromethane, chloroform. Extractions were performed using 100 mL of solvent with a piece of prepreg measuring 5 cm x 5 cm. The best solvent in terms of solubility is tetrahydrofuran; it dissolves the resin even when it is significantly advanced beyond the usual B-stage. Although it is excellent for liquid chromatography work, it is unsuitable for IR work because it associates strongly with the resin and is very difficult to evaporate completely without heating. Traces left in the resin give peaks at 1070 and 925 cm^{-1} which interfere with the peaks used for quantitative analysis (discussed in Section 3.3). The association probably occurs through hydrogen bonding with the NH_2 groups of the DDS, because the N-H stretching peaks in the 3500-3200 cm^{-1} region are much broader than they are in the case of the other solvents mentioned. Further evidence of such association was obtained by size-exclusion chromatography, as discussed in a subsequent report (Part 3 of this series). The next best solvent to THF in terms of solubility, and the best for IR work, is acetone. It readily dissolves typical B-stage resin, it is easily removed by evaporation under vacuum, and even if traces remain, the major peaks do not coincide with the main peaks used for resin analysis. When acetonitrile is used to extract the resin, the solution is initially cloudy but clears after standing for about ten minutes. This indicates that the resin solubility is approaching the limit. Chloroform and

dichloromethane are worse still, giving solutions which remain slightly cloudy permanently. Hence they are not recommended.

3.3 The Infrared Spectrum of Narmco 5208 Resin

Figure 3 shows the transmission infrared spectrum of a thin film of Narmco 5208 resin obtained by extracting prepreg Batch 1010 with acetone, casting on a potassium bromide window, and evaporating the acetone under vacuum. Figure 4 shows the same spectrum after conversion to absorbance units (Section 3.1) and correction of the baseline. Figures 5, 6, and 7 show the spectra of what are believed to be the main components of the system. Table 1 lists the major bands in the 5208 spectrum together with their assignment, where this is known [17, 18, 19]. The minor epoxy resin has strong bands at 1508, 1246, 1034, and 831 cm^{-1}; because the amount is small, only the 1034 cm^{-1} band appears as a distinct (but very weak) peak in the Narmco 5208 spectrum.

For quantitative analysis, either peak height or peak area can be used as a measure of intensity. With non-computerized instruments, peak heights are easier to determine. With computerized instruments, peak areas are easily calculated and are believed to be a better indicator of intensity because any variations in band width which may occur are expected to affect the peak area less than the peak height.

The bands of greatest interest for quantitative analysis are shown in detail in Figure 8. The first is the aromatic ring band at 1517 cm^{-1}, which arises mainly from the major epoxy; small contributions from the hardener and the minor epoxy are responsible for the shoulder around 1500 cm^{-1}. This band is the most suitable for use as an "internal standard". The second band of interest is really a group of bands at 1146, 1105, and 1073 cm^{-1} arising from the hardener. They are related to the sulphone group, which is not destroyed in the curing reaction, so they do not disappear on curing. The ratio of their area to that of the internal standard is thus an indicator of the total amount of hardener in the system, either free or crosslinked. The calculation can be done using either the 1146 cm^{-1} peak alone ("single sulphone") or a combination of all three ("multiple sulphone"). The third group of peaks of interest occurs between 1000 and 900 cm^{-1} and arises from unreacted epoxy rings. These peaks disappear when the epoxy rings react on curing, so they are an indicator of the amount of unreacted epoxy in the system. Peaks in this region have long been used to determine epoxy content or follow the cure [20-22]. In MY 720 a series of peaks is observed, with maxima at 906, 952, and 974 cm^{-1}, while in SU-8 there are only two peaks, at 914 and 972 cm^{-1}. For the 5208 resin, the calculation can be done using only the 906 cm^{-1} peak ("single epoxy") or the whole set ("multiple epoxy").

Table 1. Narmco 5208 IR spectrum band assignments

Frequency (cm^{-1})†	Origin†	Assignment
3466, 3368, 3239	H	N-H stretching
3045, 2996	E	Aliphatic C-H stretching (epoxide ring)
2920	E	Aliphatic C-H stretching
1626 (sh)	H	N-H deformation
1613	E	Benzene ring quadrant stretching
1595	H	" " " "
1517	E	Benzene ring symmetric stretching
1501 (sh)	H	" " " "
1384	E	
1335	E	
1293	H	Asymmetric SO_2 stretching
1256	E	
1234	E	
1190	E	
1146	H	Symmetric SO_2 stretching
1105	H	C-S stretching
1073	H	
1034	E'	
973, 952, 906	E	Epoxide ring vibrations
830	E, H	Benzene ring C-H wagging
806 (sh)	E	Epoxide ring vibration
754	E	
721	H	Benzene ring vibration
694	H	
554	H	

† E = major epoxy, H = hardener, E' = minor epoxy, sh = shoulder

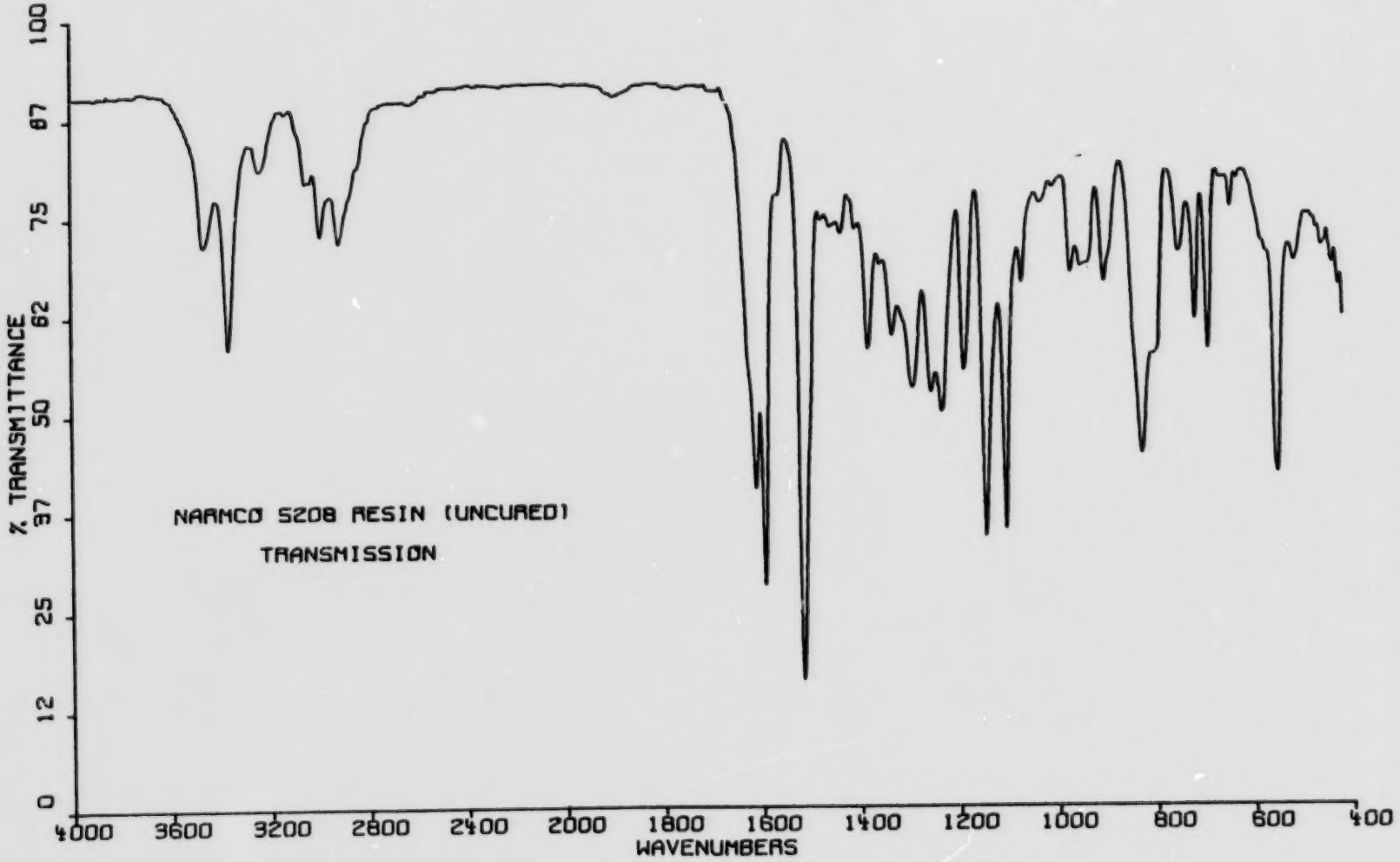


Figure 3 - Transmission IR spectrum of Narmco 5208 resin (Batch 1010, uncured). Thin film cast from acetone solution.

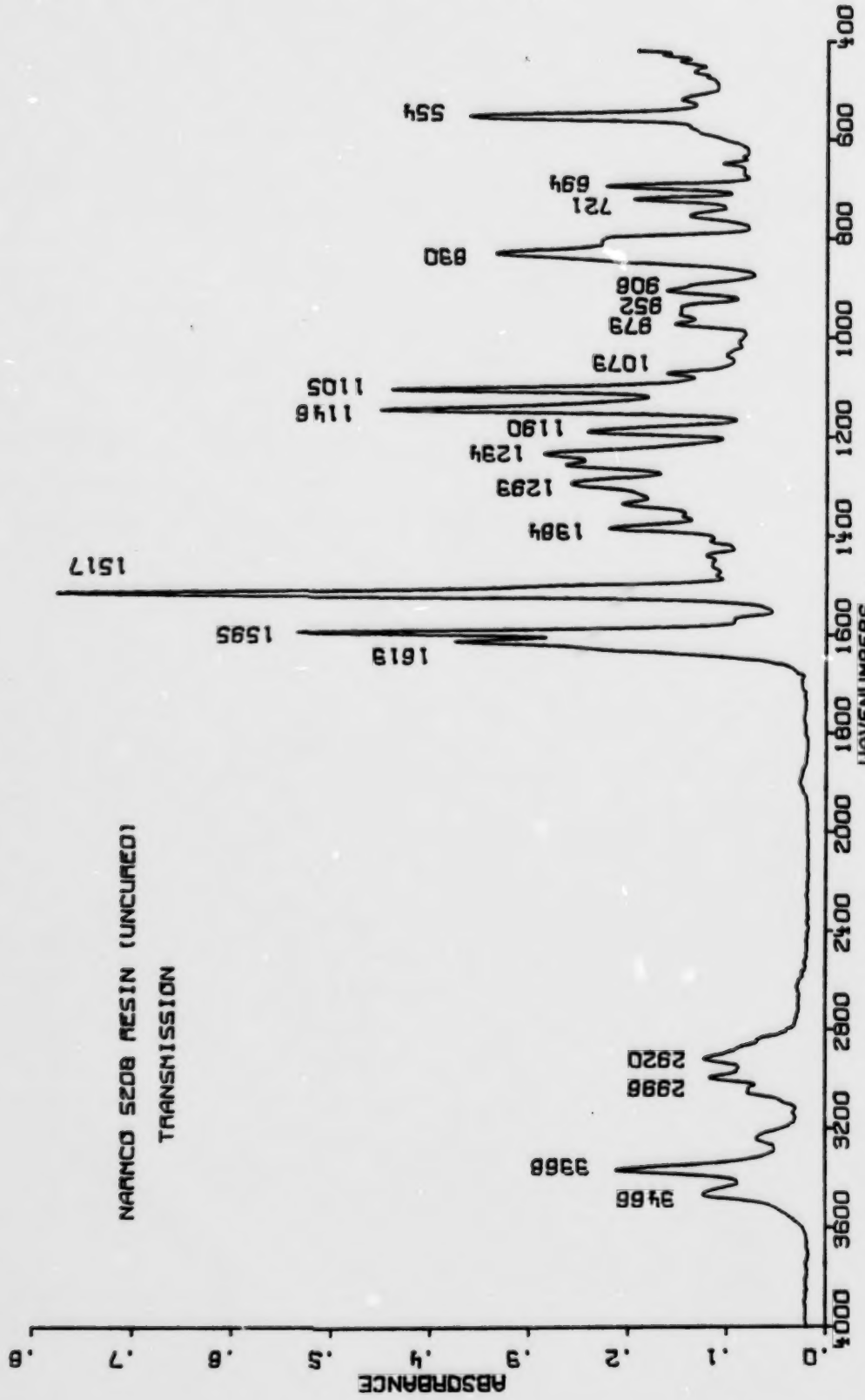


Figure 4 - Transmission IR spectrum of Narmco 5208 resin (Batch 1010) after conversion to absorbance units.

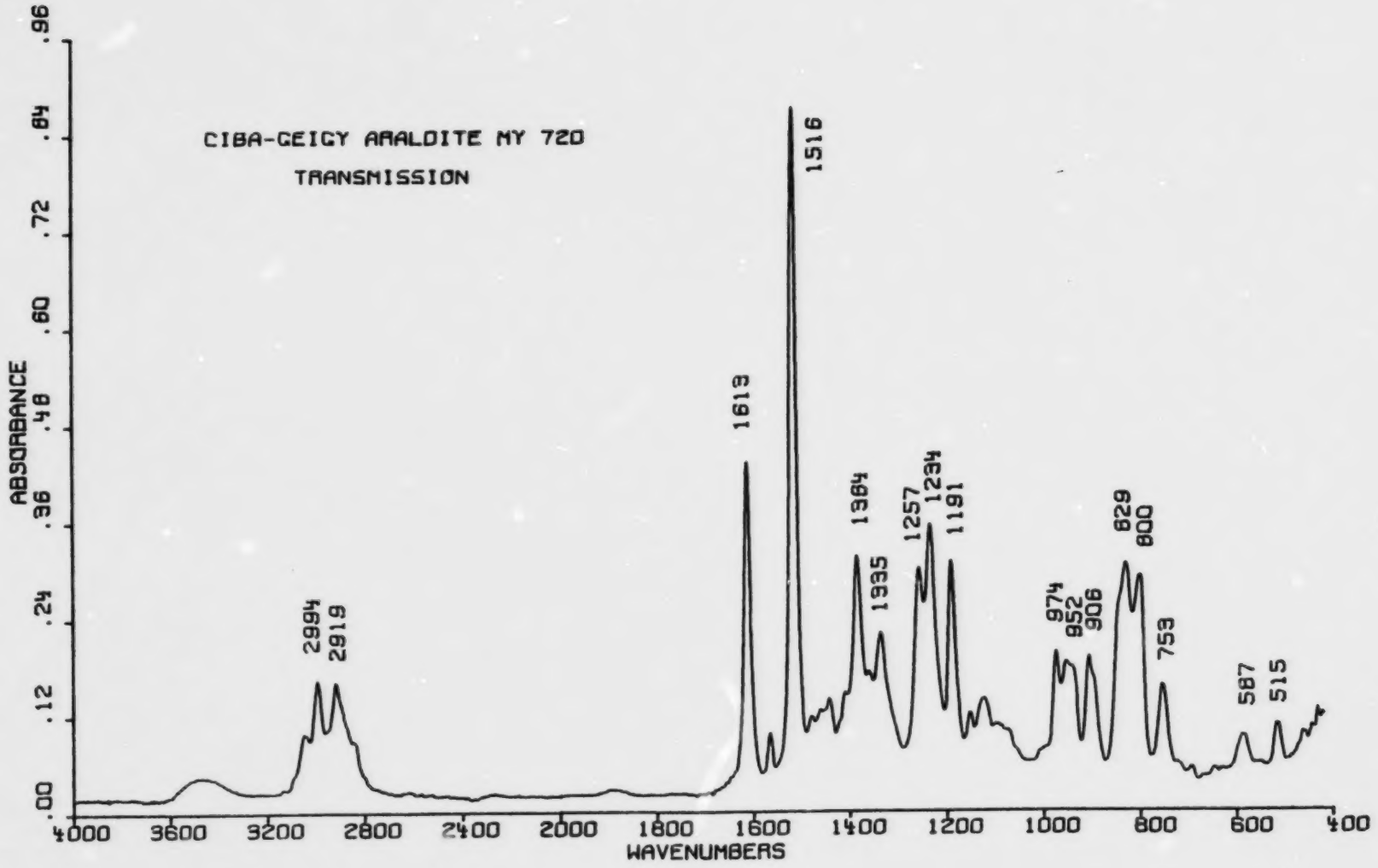


Figure 5 - Transmission IR spectrum of Ciba-Geigy Araldite MY 720 (TGDDM) epoxy resin. Thin film cast from acetone solution.

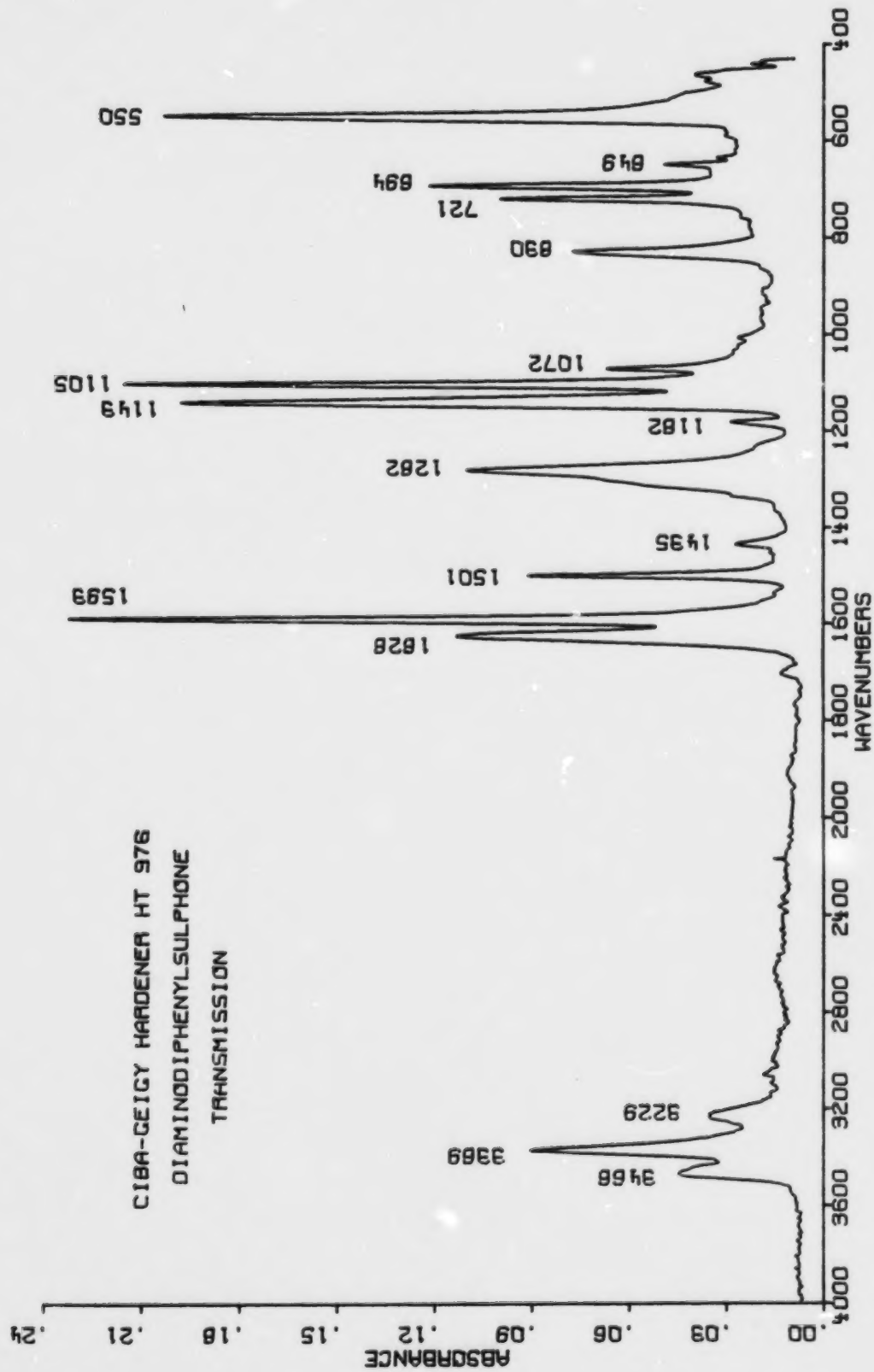


Figure 6 - Transmission IR spectrum of Ciba-Geigy Hardener HT 976 (DDS).
Thin film cast from acetone solution.

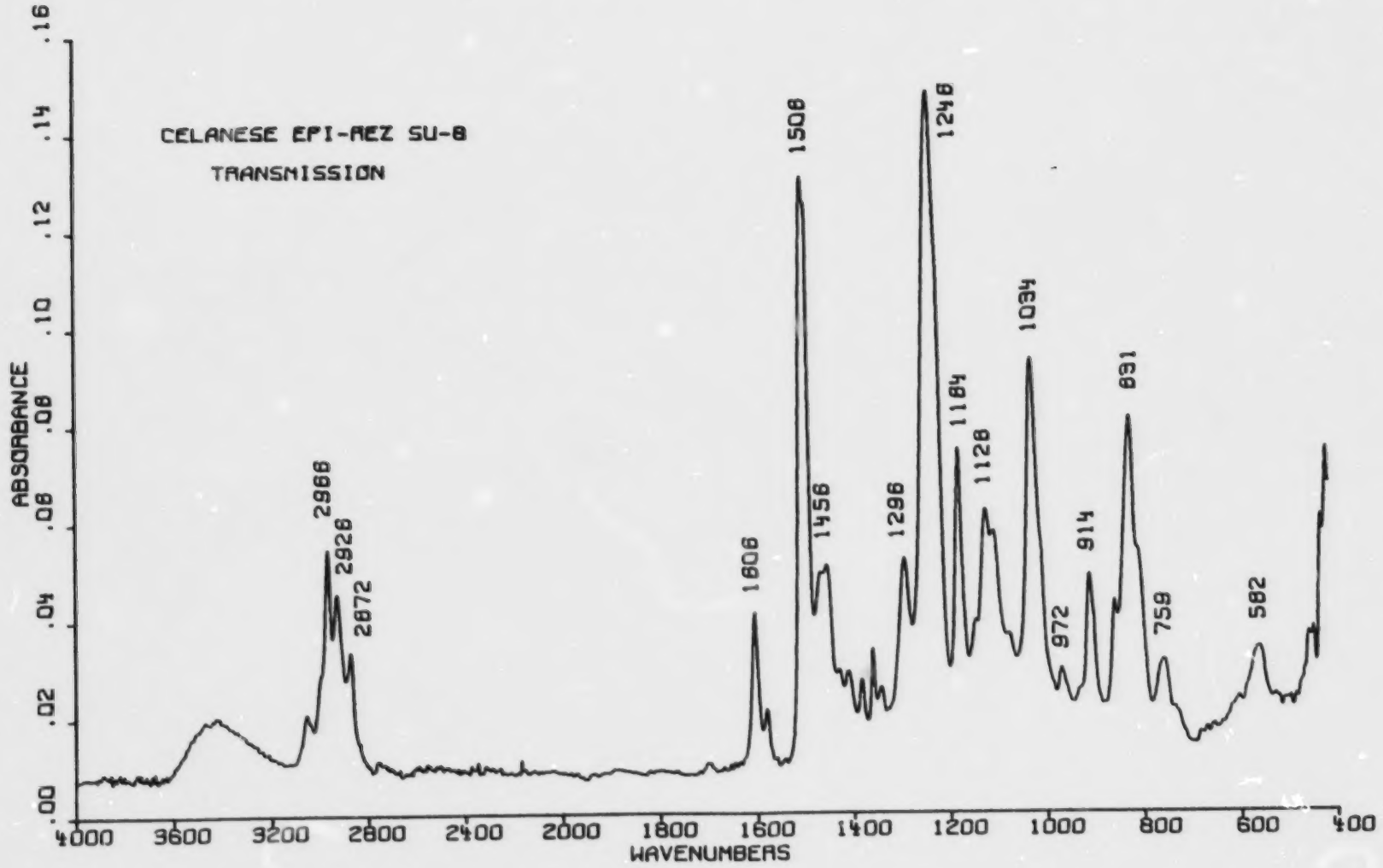


Figure 7 - Transmission IR spectrum of Celanese Epi-Rez SU-8 epoxy resin (bisphenol A Novolac epoxy).
Thin film cast from acetone solution.

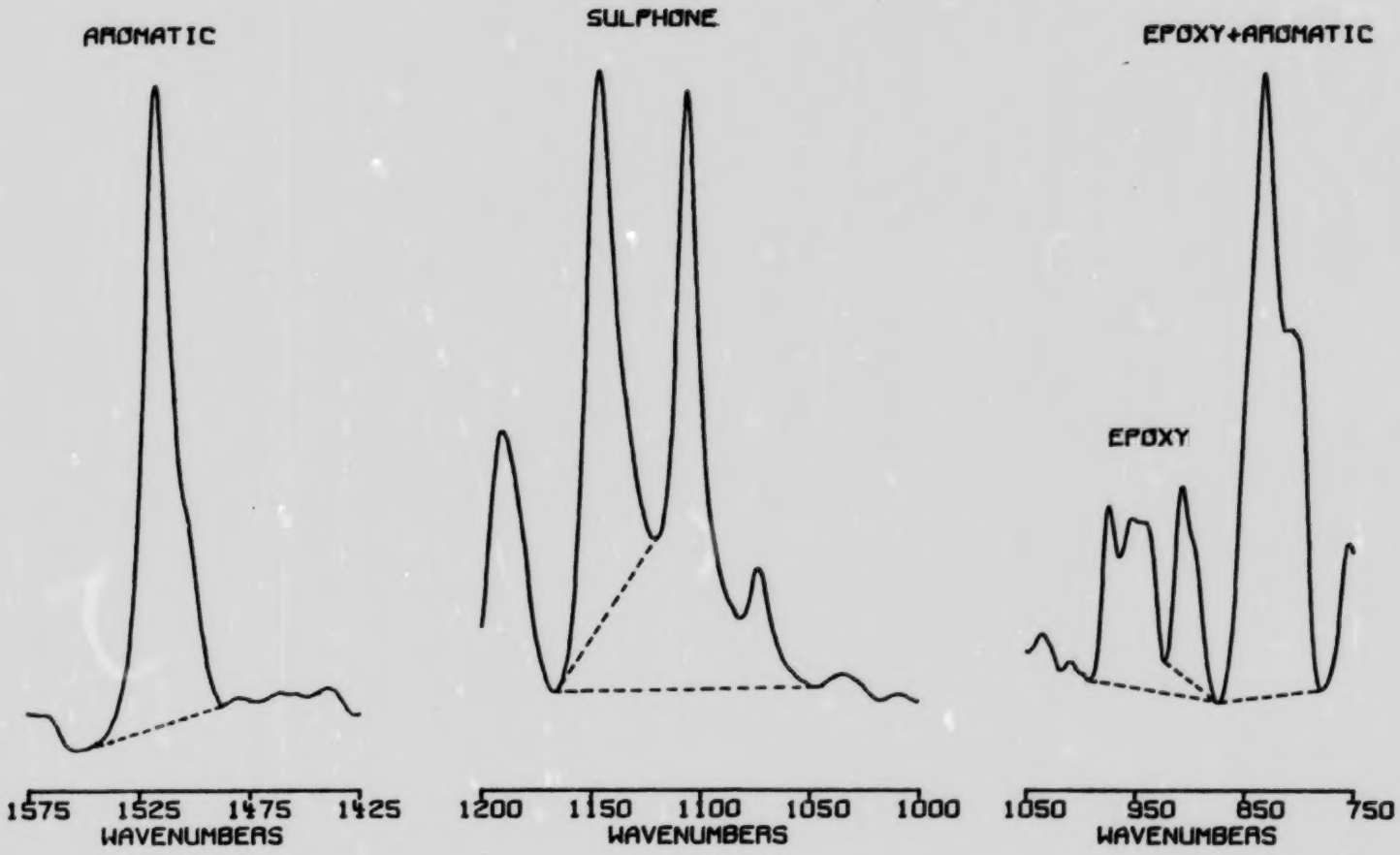


Figure 8 - Absorption bands used for quantitative analysis of Narmco 5208 resin.

Finally, there is a band at 830 cm^{-1} which is of lesser interest because it is a combination of several bands arising from aromatic ring C-H wagging and epoxide ring vibrations. All three components of the resin contribute to it.

The baselines used in calculating the peak areas are shown in Figure 8. The area under the peak and above the baseline was calculated using the Nicolet software. The quantities calculated by taking the ratio of the area (or height) of a given band against that of the "internal standard" aromatic band are henceforth referred to by the term "index" (single sulphone index, multiple sulphone index, etc.). It must be emphasized that these indices are somewhat empirical. Band shapes and intensities are affected to some extent by the molecular environment of the absorbing group. They may change, for instance, as the degree of advancement changes through aging or curing. Also, since the internal standard band contains contributions from all three components of the resin, it will be influenced to some extent by variations in composition. Thus the calculated indices are not an absolute measure of the quantity of material involved, that is, they are not necessarily directly proportional. Nevertheless, they are a very good indicator. Any increase in the amount of hardener at the expense of epoxy should result in an increase in the sulphone index. Likewise, any decrease in the number of free epoxy groups will be reflected in a decrease in the epoxy index.

The IR spectrum of the cured resin is shown in Figure 9. This was obtained using a thin film of resin (from prepreg Batch 1010) cured between two KBr disks for two hours at 135°C followed by three hours at 177°C. Comparison with Figure 4 shows several significant changes. The N-H stretching bands (3500-3200 cm^{-1}) have been largely replaced by a broad O-H band centred around 3400 cm^{-1}. In the C-H stretching region (3100-2800 cm^{-1}) the band shape has changed because of the disappearance of the epoxy peak at 2996 cm^{-1}. The epoxy peaks in the 1000-900 cm^{-1} region have also practically disappeared. The shoulder at 1626 cm^{-1} due to N-H deformation has vanished as a result of reaction of the N-H groups, and the peak at 1613 cm^{-1} has merged with the 1595 cm^{-1} band, increasing its apparent intensity. The "internal standard" aromatic ring band at 1517 cm^{-1} has shifted to slightly lower frequency (1514 cm^{-1}) and broadened somewhat, so that the shoulder at 1501 cm^{-1} (which can be seen in Figure 8) is no longer evident at all. The sulphone bands remain at much the same frequencies (1145 and 1106 cm^{-1}) but their relative intensities change. Gupta et al. [23] have related this to the transformation of the primary amine groups into secondary ones. The combination "epoxy + aromatic" band has changed shape due to the loss of epoxy groups and its maximum has shifted from 830 to 820 cm^{-1}. Other changes in the spectrum include the appearance of two new peaks at 1722 and 1666 cm^{-1}. These are due to carbonyl groups formed through oxidation of the resin.

As a consequence of the above, it can be seen that the infrared spectrum readily

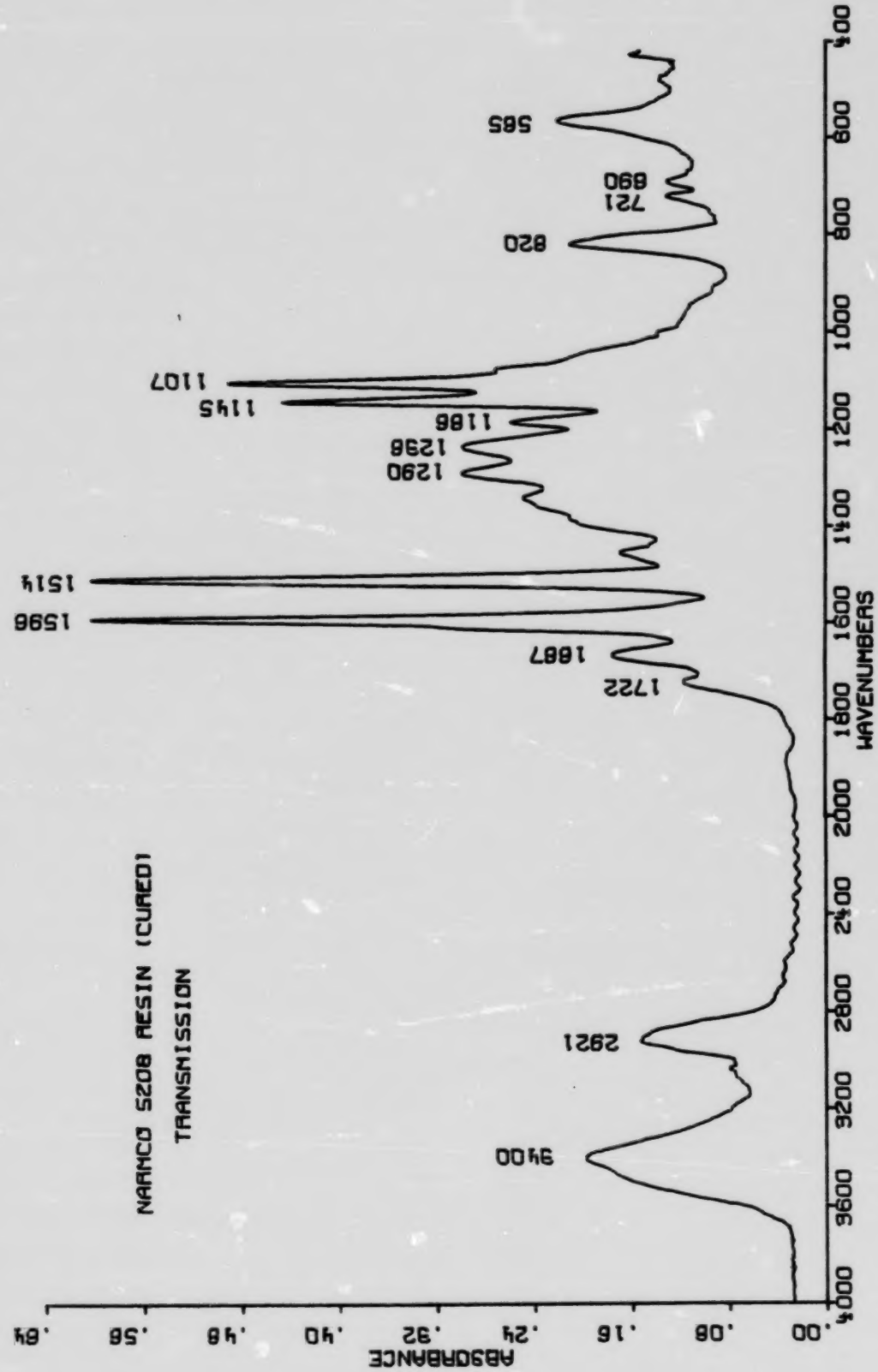


Figure 9 - Transmission IR spectrum of Narmco 5208 resin Batch 1010 (cured).

serves four useful purposes:

(a) As a "fingerprint" of the resin it can be used to detect contamination (new peaks) or significant changes in the resin composition.

(b) The sulphone bands at 1146 and 1105 cm^{-1} can be used to quantify the total hardener content of the resin.

(c) The epoxy bands in the 1000-900 cm^{-1} region can be used to quantify the content of unreacted epoxy, to follow the curing of the resin, and to confirm completeness of cure.

(d) The appearance of carbonyl bands near 1722 and 1666 cm^{-1} can be used to detect degradation due to oxidation.

3.4 Quantitative Analysis

An experiment was performed to evaluate the precision of the quantitative method outlined in the previous section. A square of prepreg from Batch 1010 measuring approximately 5 cm by 5 cm was extracted with 20 mL of acetone in two stages (15 mL + 5 mL). This gives a solution with a resin concentration of about 30 mg/mL. Ten different specimens were prepared by depositing a few drops of the solution on a KBr window, blowing with a stream of air from a rubber bulb to remove most of the solvent, and drying under vacuum (without heat) to remove the remainder of the solvent. The IR spectra were recorded and converted to absorbance. The areas of the five most useful bands shown in Figure 8 were calculated using Nicolet software with the following integration limits:

Aromatic ring (reference)	1550 - 1485 cm^{-1}
Single sulphone	1166 - 1120 cm^{-1}
Multiple sulphone	1166 - 1048 cm^{-1}
Single epoxy	923 - 875 cm^{-1}
Multiple epoxy	993 - 875 cm^{-1}.

To eliminate the effect of the sample thickness, the areas of the sulphone and epoxy bands were divided by the area of the aromatic ring reference band. This gives ratios which are

indicators of the amounts of sulphone and epoxy respectively. The results are summarized in Table 2. Surprisingly, an enormous variation is observed, with standard deviations of 10% for the sulphone bands and 28% for the epoxy bands. This is obviously unacceptable for the present application and is much higher than expected considering the photometric accuracy of modern IR instruments.

Table 2. Quantitative analysis of Narmco 5208/WC3000 prepreg Batch 1010 by IR transmission (first experiment)

Specimen	Index = Band area divided by area of aromatic reference band			
	Single sulphone	Multiple sulphone	Single epoxy	Multiple epoxy
1	0.437	1.105	0.144	0.439
2	0.451	1.233	0.142	0.435
3	0.458	1.247	0.150	0.452
4	0.474	1.449	0.275	0.838
5	0.510	1.417	0.221	0.671
6	0.507	1.465	0.256	0.783
7	0.484	1.252	0.177	0.536
8	0.426	1.254	0.252	0.772
9	0.488	1.455	0.274	0.833
10	0.475	1.506	0.309	0.945
Average	0.471	1.338	0.220	0.670
Standard deviation	0.028 (5.9%)	0.135 (10.1%)	0.062 (28.3%)	0.191 (28.5%)

A number of factors were investigated as possible causes of the variation. These included:

(i) Choice of solvent. The experiment was repeated using chloroform and dichloromethane, but the same variation was observed. In addition, the resin solubility in

these solvents is limited, and the rapid evaporation of dichloromethane sometimes cools the sample to the point of causing condensation of atmospheric moisture.

(ii) Presence of residual solvent. No correlation was observed between the variation of the results and the presence of weak residual solvent peaks in the spectra. This was true for the chlorinated solvents as well as acetone. Also, the presence of traces of moisture in the samples prepared using dichloromethane had little effect on the results.

(iii) Method of calculation. When band ratios were calculated using peak heights instead of areas, no improvement was observed. In fact, the variation was greater.

(iv) Sample inhomogeneity. The possibility of inhomogeneity resulting from separation of resin components (for example, epoxy and hardener) during solvent evaporation was considered. However, this is unlikely since specimens which show a high epoxy index also show a high sulphone index. Also, there was no visual evidence of separation.

(v) Overall spectral intensity. A very weak correlation was observed between the calculated indices and the overall intensity of the spectrum, which is related to the sample thickness. However, this is believed to be a secondary effect related to the true reason for the variation.

(vi) Nonuniform sample thickness. As explained in the next paragraph, this was found to be the main reason for the variation of the results. The weak correlation mentioned in (v) is a consequence of the fact that with thicker samples the effect is more pronounced.

The problem of nonuniform sample thickness has been discussed by Koenig [24] and Hirschfeld [25, 26]. It is sometimes referred to as the "wedging effect" since it occurs in liquid cells in which the windows are not parallel and the sample takes the shape of a wedge. As pointed out in Section 3.1, for a sample of uniform thickness b, the "internal transmittance", or the transmittance of the sample itself neglecting reflection effects at the boundary surfaces, is given by the Beer-Lambert law:

$$T = 10^{-abc} = e^{-kb}$$

where k, known as the absorption coefficient, is related to a and c by the relation $k = ac \ln 10$. If, however, the sample thickness within the area covered by the IR beam varies uniformly over a range δ (i.e. from $b - 1/2\,\delta$ to $b + 1/2\,\delta$), it can be shown [24-26] that the apparent transmittance T' will be given by:

$$T' = e^{-kb} \times \frac{e^{\frac{1}{2}k\delta} - e^{-\frac{1}{2}k\delta}}{k\delta}$$

where b is now the average thickness. The apparent absorbance A' may be expressed in terms of the "true" absorbance A by the following equation:

$$A' = A - \log_{10}\left\{\frac{10^{\frac{1}{2}\frac{\delta}{b}A} - 10^{-\frac{1}{2}\frac{\delta}{b}A}}{\frac{\delta}{b}A \ln 10}\right\}$$

The effect is shown graphically in Figure 10. The apparent absorbance is always lower than the true absorbance and the deviation is greatest when the absorbance is high (i.e. for strongly absorbing bands and for thick samples) or when the thickness variation is high. The effect on the appearance of the spectrum is to produce an apparent suppression of the stronger bands. This is illustrated in Figure 11, which shows two spectra from the series used to calculate the results given in Table 2. The lower spectrum (from specimen 1) is one for which the thickness variation is believed to be low, whereas the upper one (from specimen 4) shows evidence of a substantial variation, which may be seen by looking at the aromatic ring band at 1517 cm^{-1}. In the upper spectrum, this band appears relatively less intense when compared to weaker bands such as the epoxy bands at 1000-900 cm^{-1}, due to the "suppression" mentioned above. In Figure 12, the absorbance at the band maximum in the spectrum of specimen 4 is plotted against the corresponding absorbance for specimen 1 for most of the bands in the spectrum. If both specimens were of uniform thickness, the two spectra would be identical in appearance (although not in absolute intensity), and the plot would be a straight line with slope equal to the ratio of the two thicknesses. Instead, a smooth curve is obtained whose form resembles that of the curves shown in Figure 10. This provides strong evidence that the deviations in the spectra are the result of a variation in sample thickness.

Since the degree of suppression is related to the band intensity, stronger bands such as the aromatic ring band will be affected more than weaker ones such as the sulphone and epoxy bands. As a result, the calculated indices given in Table 2 will always be artificially high if there is a thickness variation effect. The most reliable results in Table 2 are therefore those with the lowest values, namely specimens 1, 2, 3, and 7.

This also explains why a greater standard deviation is observed when peak heights

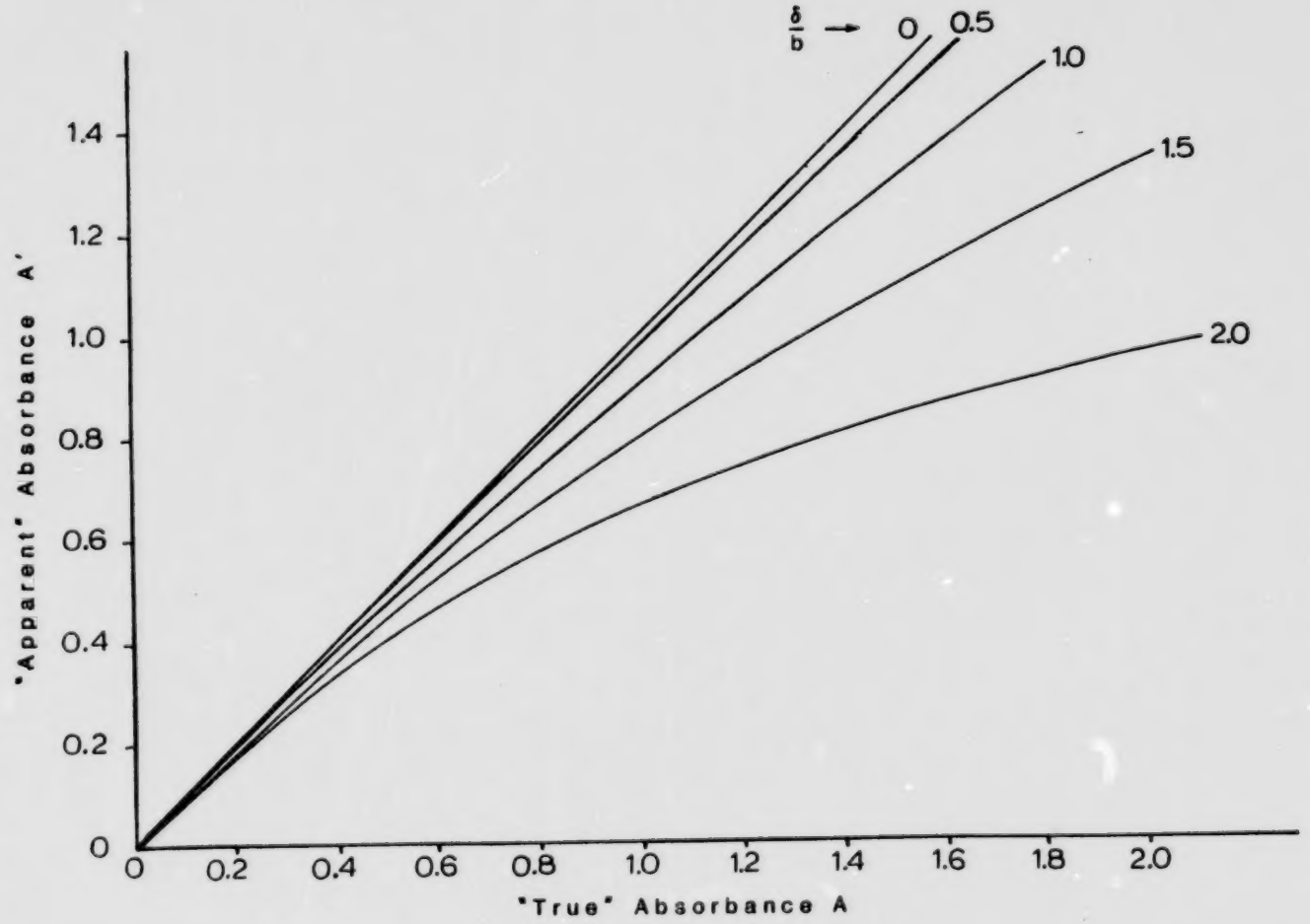


Figure 10 - Effect of sample thickness variation on measured absorbance.

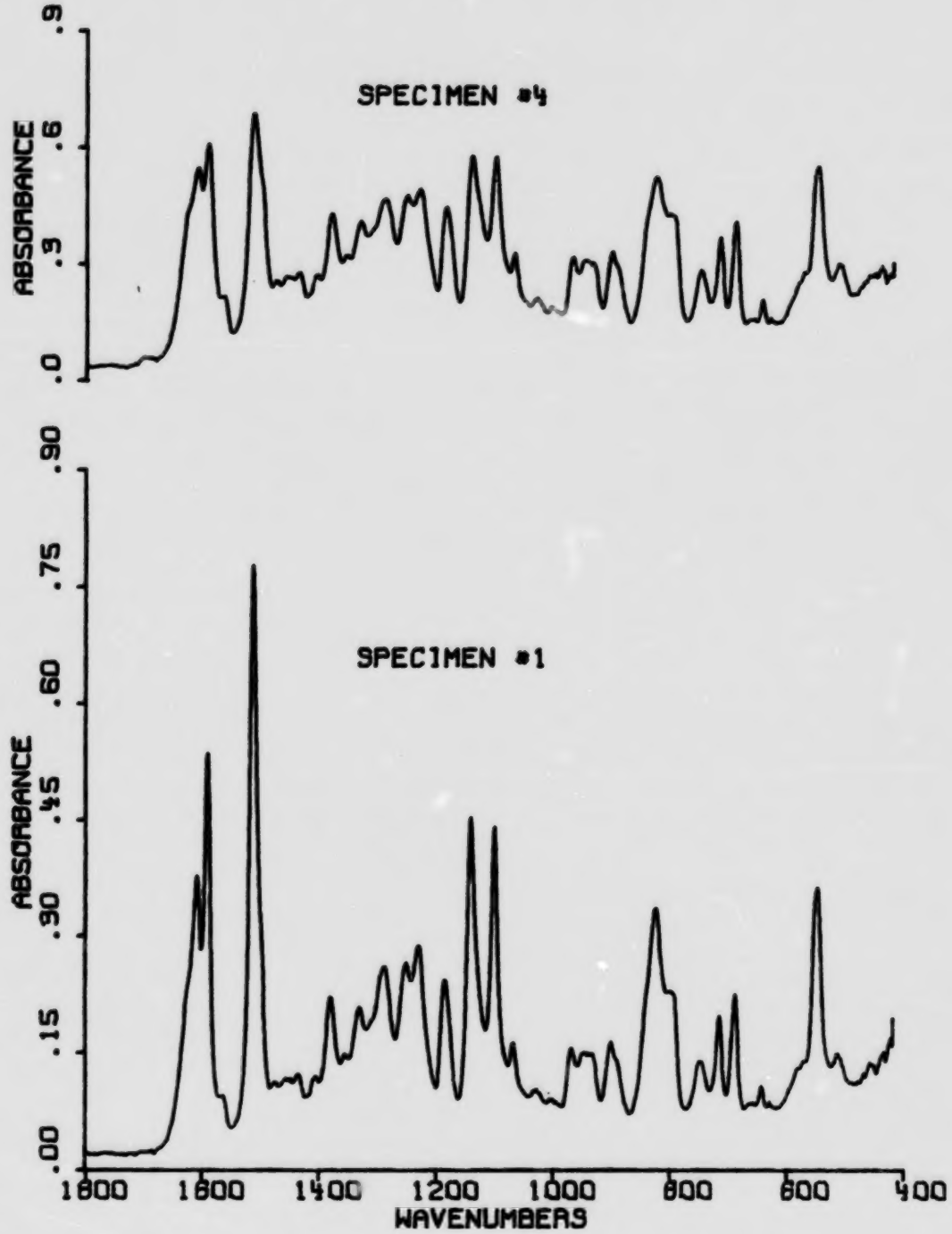


Figure 11 - Transmission IR spectrum of Narmco 5208 resin:
Specimen # 1 - film of uniform thickness;
Specimen # 4 - film of varying thickness.

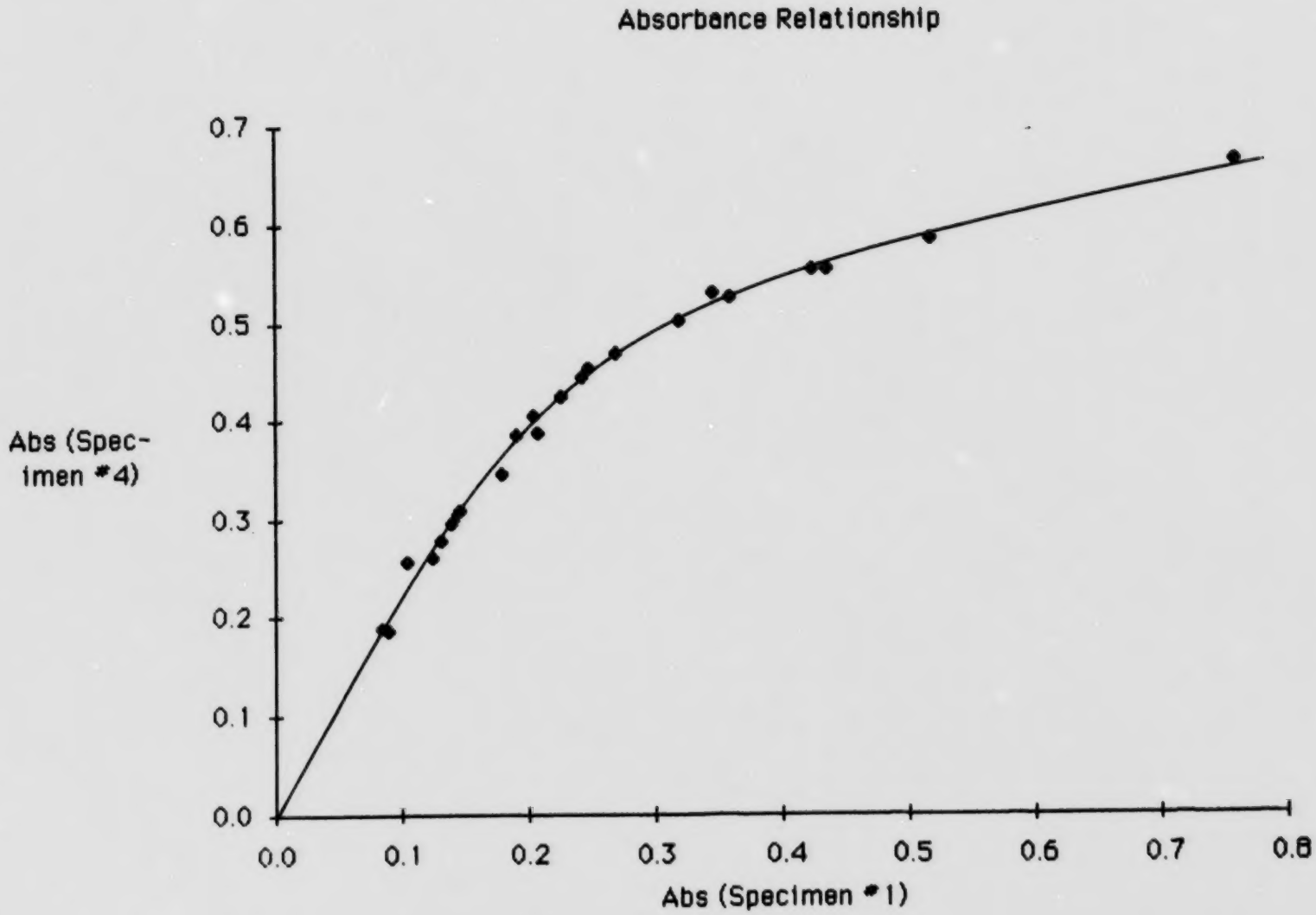


Figure 12 - Relationship between peak absorbance values for specimens # 4 and # 1 (see Figure 11)

are used for the calculation instead of peak areas. Peak heights are calculated on the basis of only one point, the point of maximum intensity, which is also the point where the deviation due to the thickness variation is at a maximum.

In an attempt to overcome the problem of thickness variation, the initial experiment was repeated using greater care in sample preparation. For example, the bulk of the solvent was left to evaporate by itself rather than subjected to a stream of air. Five specimens were measured and the results are summarized in Table 3. The reproducibility is much better than in the initial experiment. Specimen 2 gives significantly higher results than the four others, indicating a thickness variation effect. If this sample is eliminated from the averaging, the standard deviations drop to 2.5% or less.

Table 3. Quantitative analysis of Narmco 5208/WC3000 prepreg Batch 1010 by IR transmission (second experiment)

Specimen	Index = Band area divided by area of aromatic reference band			
	Single sulphone	Multiple sulphone	Single epoxy	Multiple epoxy
1	0.433	1.078	0.131	0.404
2	0.445	1.197	0.153	0.476
3	0.438	1.107	0.134	0.415
4	0.416	1.045	0.129	0.393
5	0.426	1.059	0.129	0.397
Average (all five)	0.432	1.097	0.135	0.417
Standard deviation	0.011 (2.6%)	0.060 (5.5%)	0.010 (7.5%)	0.034 (8.2%)
Average (without no. 2)	0.428	1.072	0.131	0.402
Standard deviation	0.010 (2.2%)	0.027 (2.5%)	0.002 (1.8%)	0.010 (2.4%)

A third experiment was subsequently done using Batch 1014 instead of Batch 1010. In addition to five carefully prepared specimens, two were prepared with use of an air stream from a rubber bulb to evaporate the solvent. The results are given in Table 4. For the carefully prepared samples, the reproducibility is about 2%, but the specimens prepared with blowing show deviations of greater than 60%.

Table 4. Quantitative analysis of Narmco 5208/WC3000 prepreg Batch 1014 by IR transmission

Specimen	Index = Band area divided by area of aromatic reference band			
	Single sulphone	Multiple sulphone	Single epoxy	Multiple epoxy
1	0.452	1.098	0.141	0.423
2	0.439	1.056	0.135	0.408
3	0.440	1.062	0.134	0.405
4	0.440	1.057	0.135	0.411
5	0.441	1.092	0.138	0.418
6†	0.482	1.328	0.224	0.678
7†	0.500	1.292	0.188	0.567
Average (1-5 only)	0.442	1.073	0.137	0.413
Standard deviation	0.005 (1.2%)	0.020 (1.9%)	0.003 (2.1%)	0.007 (1.8%)

†Specimens prepared with blowing to evaporate the solvent.

In conclusion, the transmission method with cast films is acceptable for IR quantitative analysis of Narmco 5208 prepreg provided care is taken to prepare films of uniform thickness. With good technique, a precision of 2% is obtainable. The

recommended procedure is described in detail in Section 3.8. The importance of uniform sample thickness does not appear to have been recognized in previous work on analysis of epoxy resins. This may explain why in some cases a high degree of scatter has been observed [27], and why some workers feel that infrared spectroscopy is of value only as a qualitative tool [28]. The results shown here demonstrate that this is not the case.

3.5 Comparison of Different Batches

The seven different batches of Narmco 5208 resin described in Section 2.1 were analysed using the procedure developed as outlined above. The results obtained are given in Table 5.

Table 5. Quantitative analysis of different batches of Narmco 5208 by IR transmission spectroscopy

Batch No.	Index = Band area divided by area of aromatic reference band			
	Single sulphone	Multiple sulphone	Single epoxy	Multiple epoxy
1010	0.426 (0.004)	1.047 (0.011)	0.130 (0.001)	0.391 (0.005)
1014	0.436 (0.002)	1.052 (0.005)	0.136 (0.001)	0.408 (0.002)
1101	0.424 (0.002)	1.022 (0.007)	0.134 (0.001)	0.395 (0.002)
1103	0.424 (0.001)	1.045 (0.007)	0.127 (0.001)	0.375 (0.001)
1104	0.429 (0.003)	1.037 (0.008)	0.129 (0.001)	0.380 (0.002)
1047	0.448 (0.005)	1.087 (0.015)	0.136 (0.003)	0.411 (0.007)
1023	0.427 (0.004)	1.099 (0.012)	0.123 (0.001)	0.370 (0.004)

Each result is an average over five specimens with the standard deviation shown in parentheses. In most cases the deviation is under 1%. Comparison of the different batches shows no particularly large variations. The "multiple sulphone" indices are all within ±4% of the mean (1.056), and the "multiple epoxy" indices are all within ±6% of

the mean (0.390). Nevertheless, in many cases the differences can be considered statistically significant. For the conditions used (five specimens per sample), it can be shown using standard statistical theory [29] that two indices X_1 and X_2 with respective unbiased standard deviations of S_1 and S_2 can be considered to be significantly different with a confidence level of 95% if the difference between them $|X_1-X_2|$ exceeds $1.03\sqrt{S_1^2 + S_2^2}$, or 1.46 S if $S_1 = S_2 = S$. Using this criterion and the multiple epoxy index, the batches can be arranged in order of free epoxy content as follows: 1047 ≈ 1014 > 1101 ≈ 1010 > 1104 > 1103 > 1023. The single epoxy index gives much the same result. The batch with the highest epoxy content (Batch 1047) consists of neat resin coated on a plastic sheet without graphite cloth; it is probably less highly advanced than the usual prepreg samples. Surprisingly, the batch with the lowest epoxy content also consists of neat resin, this time in bulk form. It is believed that this sample was heated to reduce its viscosity for transfer to the can in which it was shipped, and that this caused significant advancement of the resin. The sulphone indices are more difficult to interpret, since the overall variation is lower and the single and multiple indices do not follow the same order. This may be due to the fact that the sulphone bands are sensitive to effects such as hydrogen bonding and moisture absorption [17].

Transmission spectra were also recorded for cured films prepared as described in Section 3.3. All seven batches gave spectra very similar to Figure 9. No significant differences were observed.

3.6 Resin Cure

The changes occurring in the IR transmission spectrum during the cure cycle of the Narmco 5208 resin were studied using the setup described in Section 2.3. Controller and transformer settings were chosen to give a sample temperature profile which matched as closely as possible the recommended program for cure of Narmco 5208. The result is shown in Figure 13. The sample is heated to 135°C (275°F) within a one-hour period, maintained at this level for one hour, heated to 177°C (350°F) within half an hour, maintained at this level for two hours, then left to cool to room temperature.

With the cell and sample installed in the FTIR spectrometer, the heating program was begun and spectra were recorded at intervals of approximately 15 minutes using an accumulation of 32 scans (total collection time about 20 seconds). Upon completion of the experiment, the stored spectra were converted to absorbance and "corrected" by subtracting

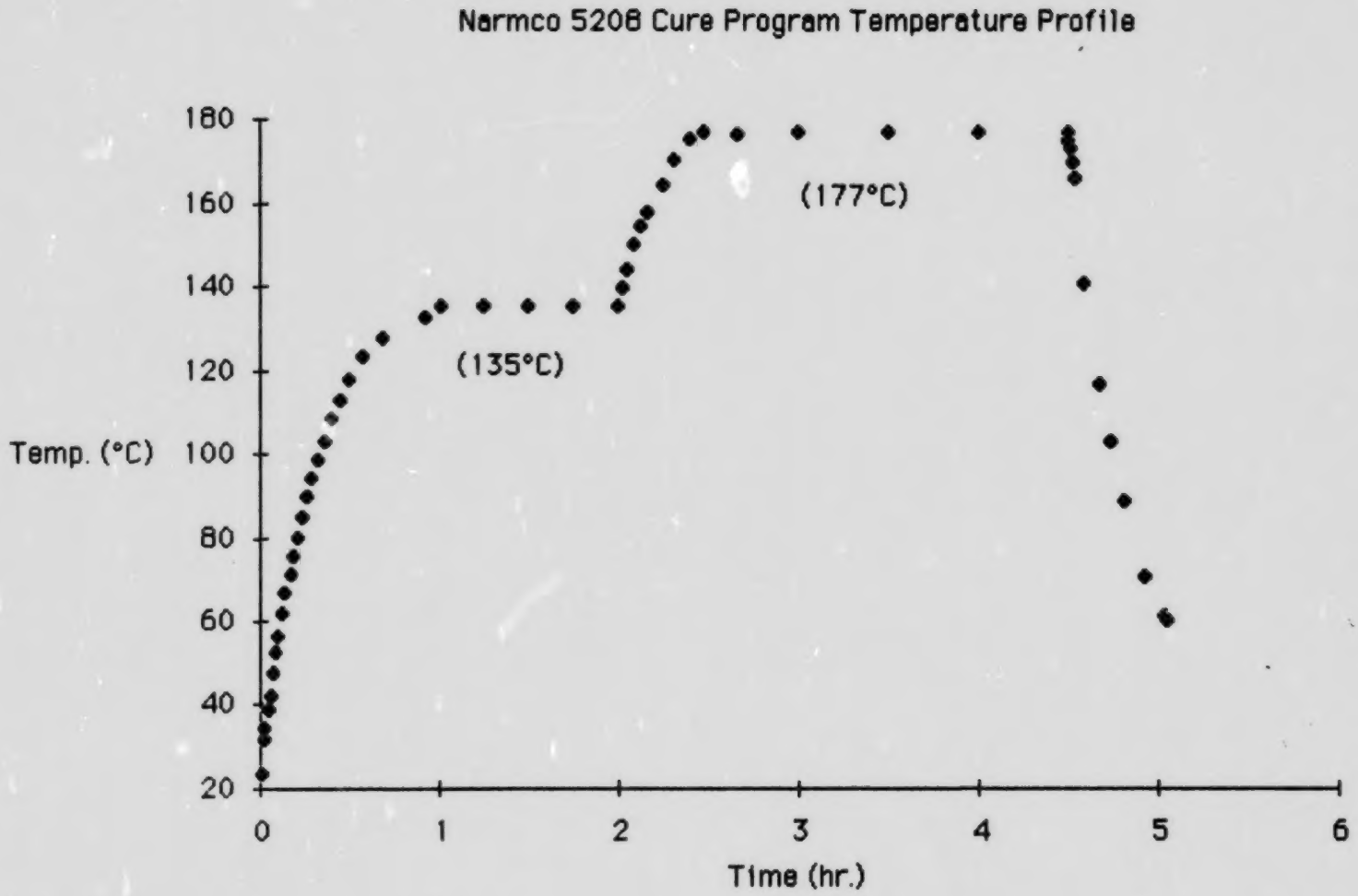


Figure 13 - Temperature program used for IR study of Narmco 5208 cure.

the spectra of the KBr windows, as well as those of any traces of water vapour or CO_2, and adjusting the baseline. The areas of the bands of interest were then calculated as described in Section 3.4. Where necessary, the limits of integration were changed slightly from those given in the recommended method to take account of changes in band shapes occurring as a result of the heating and curing. Sulphone and epoxy indices were calculated as described in Section 3.4 by taking the ratio of the appropriate band area with respect to that of the aromatic ring band at about 1517 cm^{-1}. In addition to the sulphone and epoxy bands, the combination "epoxy + aromatic" band at about 830 cm^{-1} (shown in Figure 8) was also analysed.

Two different batches of Narmco 5208 prepreg were studied: Batch 1014 and Batch 1103. Figure 14 shows the evolution of the IR spectrum during the cure of Batch 1014, and Figures 15 to 19 show the changes in the calculated indices. Although the general behaviour is the same for both batches, certain differences are apparent, for which the reasons are not clear. They may be related to the importance of uniform sample thickness, since the experiment involving Batch 1103 was done before this was discovered. For this reason, the curves for Batch 1014 are believed to be more reliable.

The sulphone indices show some variation with cure, probably related to the structural and temperature changes taking place. It has been shown that the sulphone band intensities are affected by the transformation from primary amine to secondary amine during cure [23, 30], as well as by the presence of moisture [17]. Intensities can also be affected by glass transitions [31]. The "single sulphone" index (Figure 15) appears to be more sensitive than the "multiple sulphone" index (Figure 16), which remains reasonably constant overall. Similar behaviour was observed in the aging study to be described in a later report (Part 5 of this series). The multiple sulphone index is therefore considered a better indicator of the total sulphone content.

The epoxy indices show interesting behaviour. They show that even during the first stage of the cure cycle there is significant reaction; by the end of the second hour about one-third of the epoxy groups have reacted. When the temperature is increased to 177°C, reaction occurs more rapidly, and by the end of the third hour only about 15% of the epoxy groups remain. Over the next two hours, there is further gradual reaction, but at the end of the recommended cure cycle (5 hours) there are still some unreacted epoxy groups (about 7% of the initial number). Comparison of the "single epoxy" and "multiple epoxy" curves (Figures 17 and 18) shows an interesting difference in shape at the beginning of the cure. The "single epoxy" index drops more rapidly than the "multiple epoxy" index. The reason is not obvious at this point. One possibility is that heating the resin brings about structural changes which influence the band intensities. A second possibility is a difference in

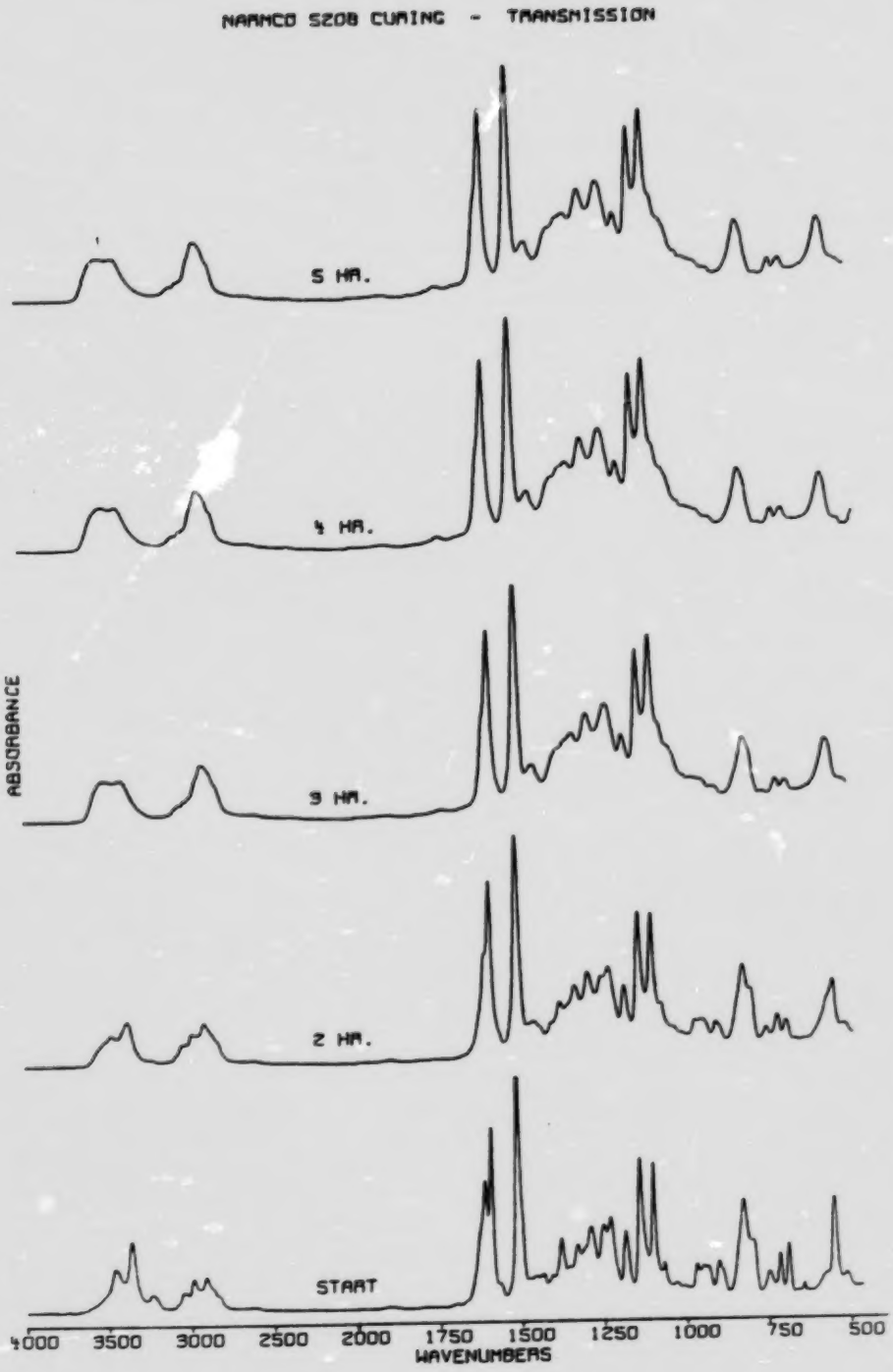


Figure 14 - Evolution of IR transmission spectrum during cure of Narmco 5208

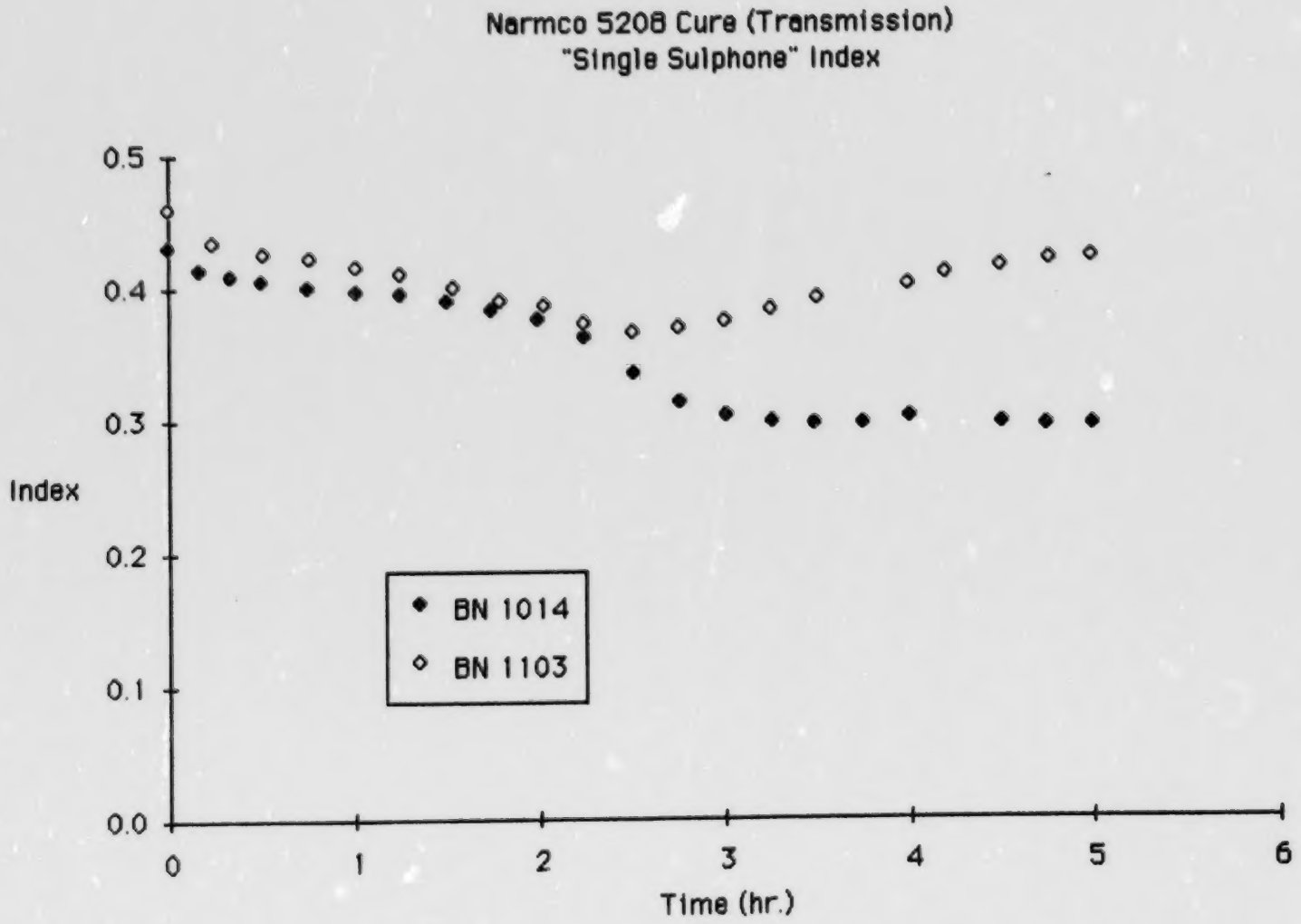


Figure 15 - Variation of "single sulphone" index as measured by IR transmission during cure of Narmco 5208 resin.

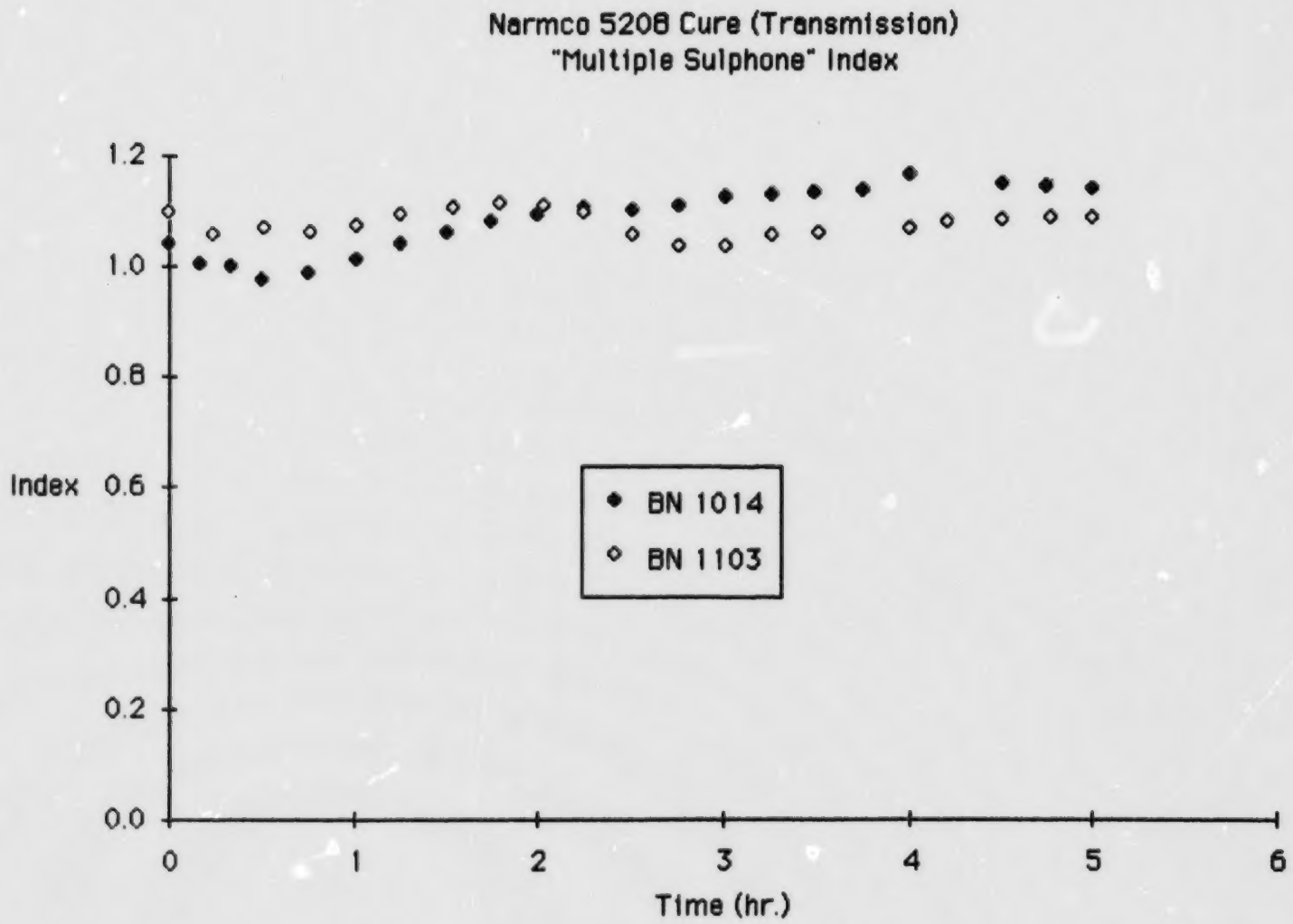


Figure 16 - Variation of "multiple sulphone" index as measured by IR transmission during cure of Narmco 5208 resin.

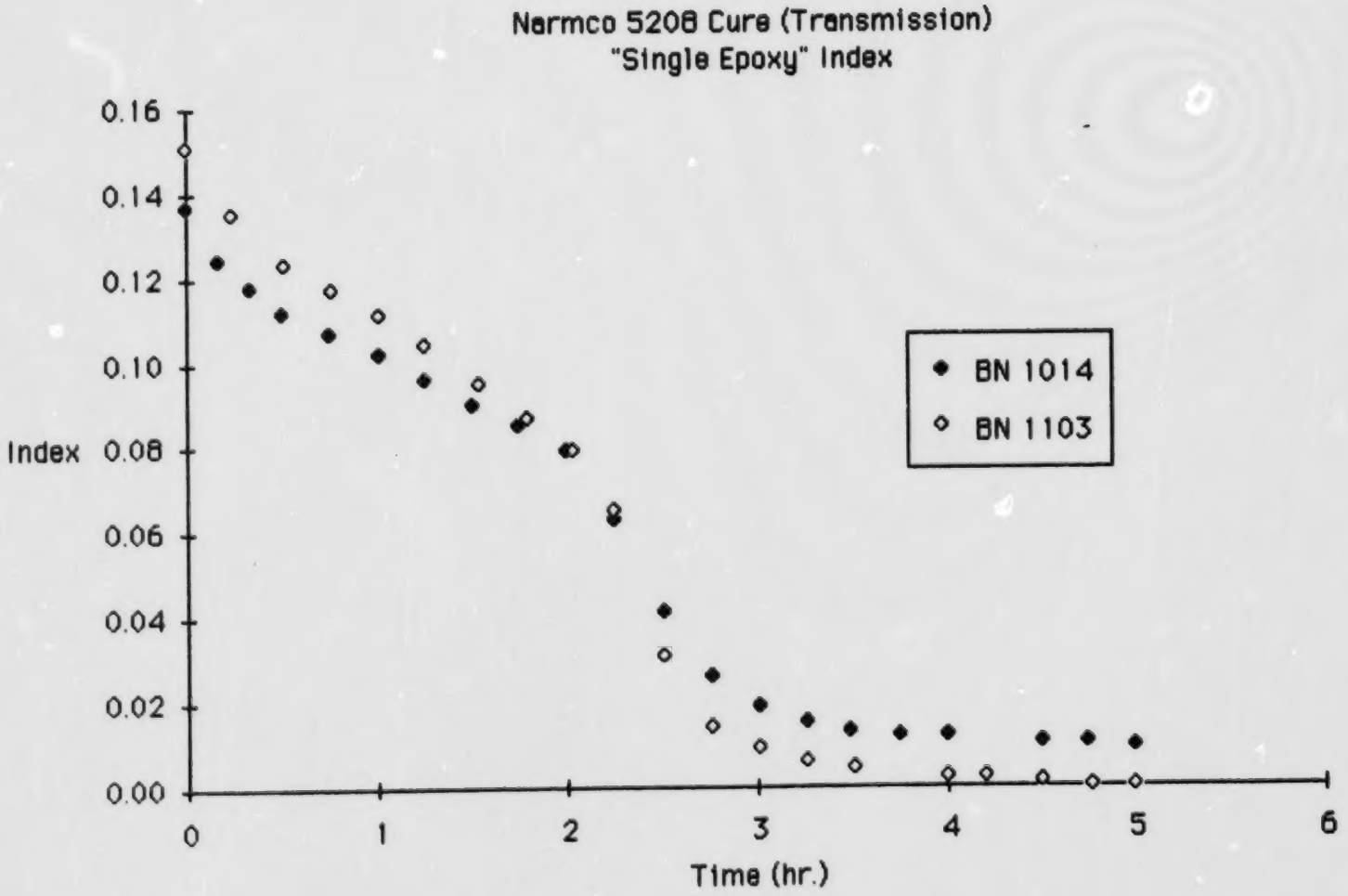


Figure 17 - Variation of "single epoxy" index as measured by IR transmission during cure of Narmco 5208 resin.

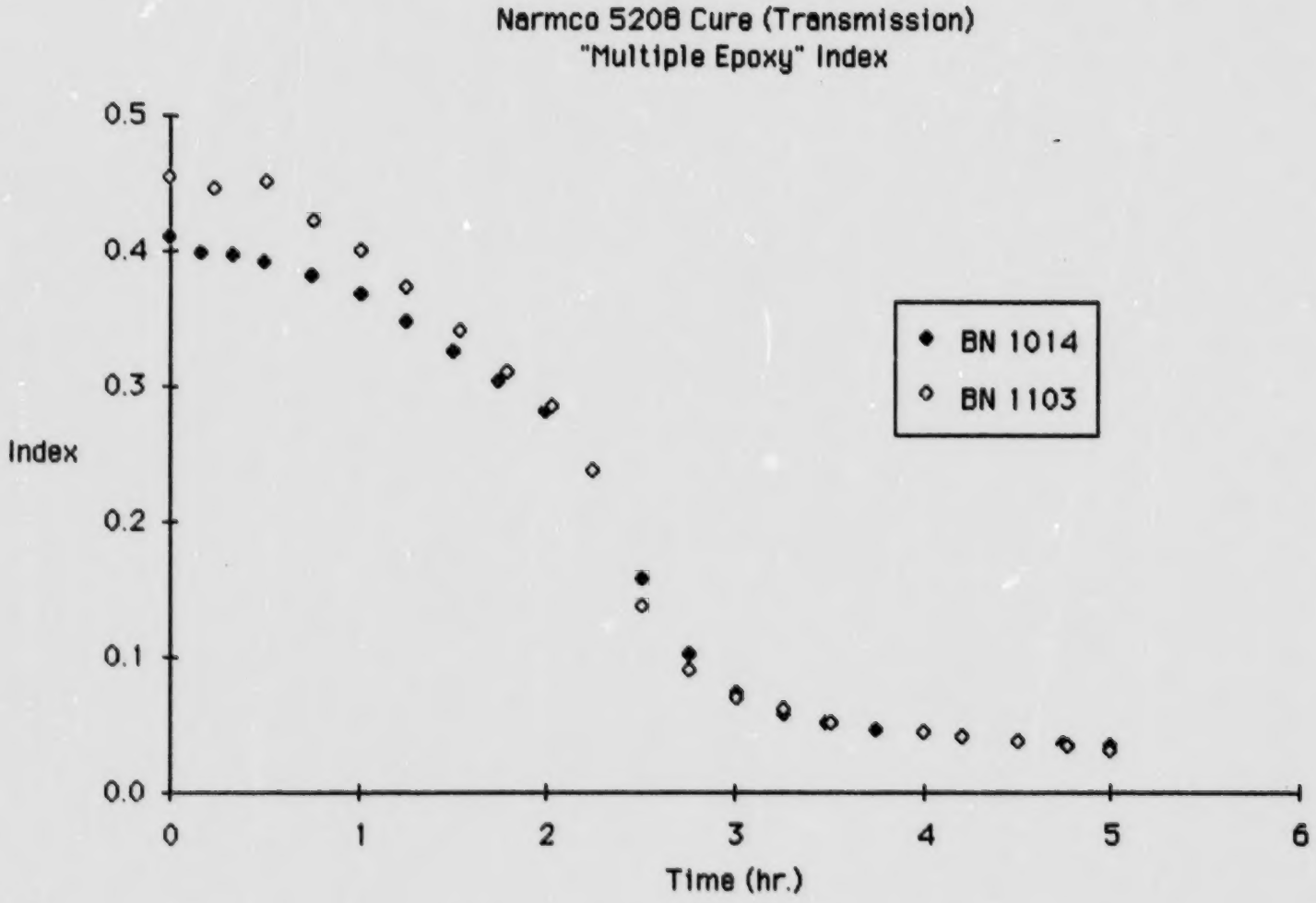


Figure 18 - Variation of "multiple epoxy" index as measured by IR transmission during cure of Narmco 5208 resin.

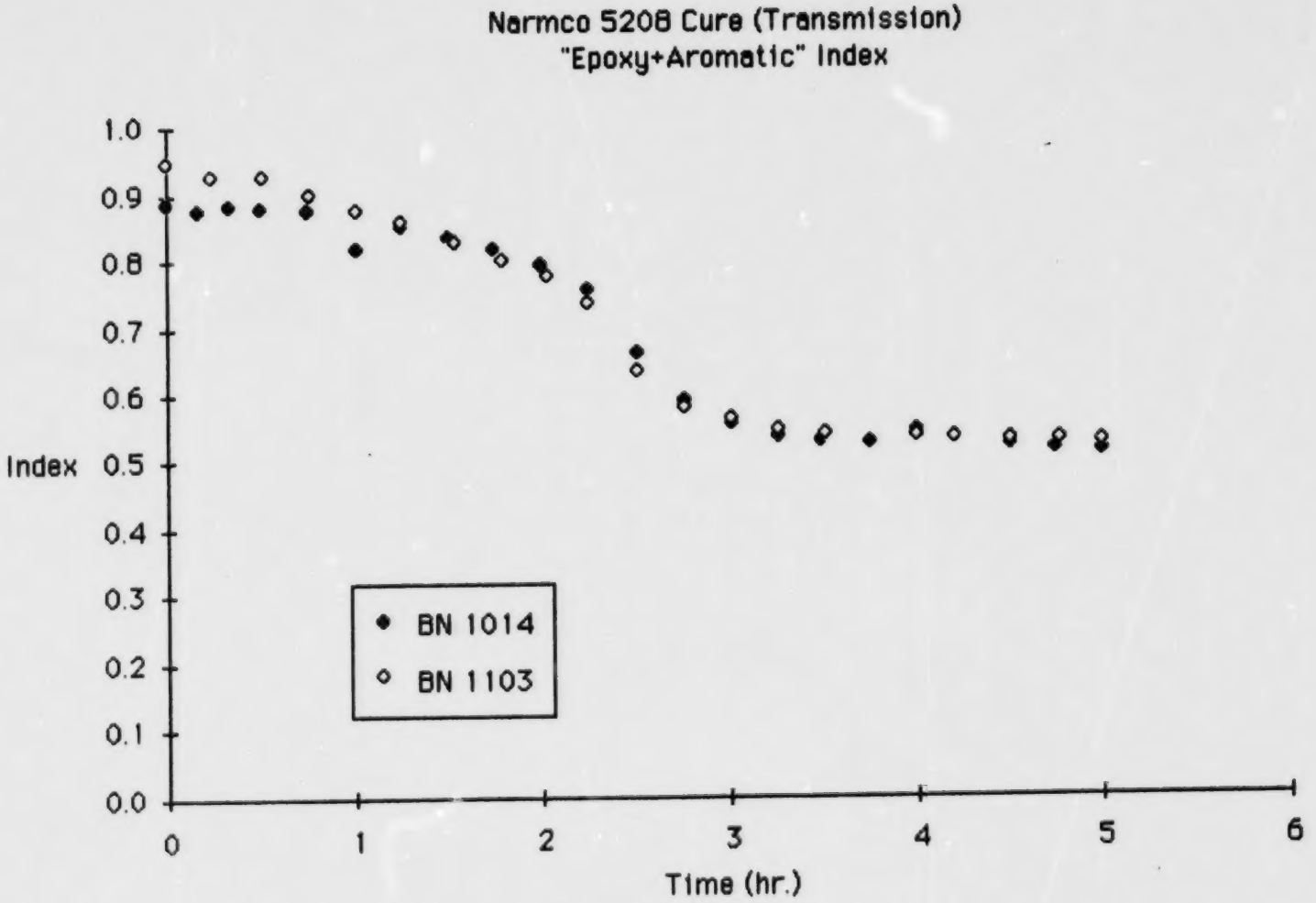


Figure 19 - Variation of "epoxy + aromatic" (band near 830 cm^{-1}) index as measured by IR transmission during cure of Narmco 5208 resin.

behaviour between the minor epoxy resin, which contributes only to the 906 cm^{-1} (single epoxy) band, and the major epoxy resin, which contributes to all three. (It has been shown [14] that the bisphenol A Novolac epoxy reacts with DDS much faster than does the TGDDM.) Whatever the explanation, the "multiple epoxy" index is considered to be a better indicator of the total free epoxy content, since it comprises all the peaks and its behaviour in the initial stages of cure (a gradual drop) is more in keeping with the behaviour expected at such low temperatures. Finally, Figure 19 shows the variation of the band near 830 cm^{-1}, which is generally considered to be an aromatic ring C-H wagging band and has been used as an internal reference instead of the 1517 cm^{-1} band to follow epoxy cure [32]. During the cure, the area of this band decreases in the same way as the epoxy bands, except that the ultimate value is not zero. This is because this band is actually a composite. The peak at 830 cm^{-1} is due to aromatic C-H wagging and appears in both Araldite MY 720 (Figure 5) and Hardener HT 976 (Figure 6). The shoulder at around 800 cm^{-1} is due mainly to epoxy rings [19] of the MY 720. The minor epoxy also contributes somewhat to both bands (Figure 7). In the Narmco 5208, the shoulder at 800 cm^{-1}, which accounts for about 44% of the band area in the two samples studied, disappears when the resin is cured and the epoxy groups react. The phenyl ring absorption remains. Because of this, this band is not really suitable for use as an "internal standard".

3.7 Near-infrared Spectroscopy

The near-IR region, located between the mid-IR and the visible, can also be used to characterize epoxy resins. Absorption coefficients tend to be much weaker than in the mid-IR, so thicker samples must be used. One advantage of this region is the low absorption of glass, which can be used as a cell material or sample support. Results have been reported for quantitative analysis of epoxy content [33, 34], the study of cure kinetics [35-37], and the analysis of moisture [17]. These analyses depend on two distinct bands, one at 4524 cm^{-1} (2.210 μm) arising from epoxy rings, and one at 5213 cm^{-1} (1.918 μm) arising from water. The 4524 cm^{-1} band is especially useful for quantitative analysis when the band near 900 cm^{-1} in the mid-infrared is subject to interference from other bands.

This region is currently of particular interest because it affords the possibility of embedding optical fibres in the organic matrix and using them as waveguides to pass a near-IR beam and probe the interior of the part. In this way, it should be possible to detect moisture penetration within the matrix, as well as monitor the extent of curing and the chemical composition in general. The method is based on the principle of internal reflection, or evanescent wave spectroscopy, which is discussed in Section 4.

To measure the near-IR spectrum of Narmco 5208 resin, a sample of prepreg Batch 1010 was extracted with acetone and a film about 0.2 mm thick was deposited on a glass microscope slide. This was then heated for 5 minutes at 110°C to remove residual acetone and give a more uniform film. The transmission spectrum was measured and the spectrum of the microscope slide subtracted to give the absorption spectrum of the uncured resin. The film was then cured by heating in an oven for 3 hours at 177°C, and the spectrum of the cured resin was measured in the same manner. The sample was then immersed in boiling water for five hours to saturate the cured resin with moisture. In the course of this treatment the film became detached from the slide. It was removed from the water, quickly wiped to remove surface moisture, rapidly weighed, and inserted in the spectrometer, where the spectrum was measured immediately. Finally, the sample was dried at 110°C for 3.5 hours and weighed again to determine the moisture content, which was found to be 5.0%.

The three spectra, measured using the Nicolet FTIR, are shown in Figure 20. The uncured resin shows a strong epoxy peak at 4524 cm^{-1}, as well as a second strong peak at 4054 cm^{-1}. In the cured resin, the epoxy band is much less intense but is still present, indicating that there are still some unreacted epoxy groups. (Further curing for 2 hours at 200°C reduced the intensity of this peak but it still did not disappear.) The 4054 cm^{-1} peak remains strong in the cured resin and could be used as a reference peak. The moisture-saturated cured resin gives essentially the same spectrum as the dry cured resin except for a very obvious water peak at 5213 cm^{-1}. When the sample was redried, this band disappeared completely.

Spectra were also recorded on a Cary 17 spectrometer, which covers the complete near-IR region from 0.7 to 2.5 μm (14300-4000 cm^{-1}). These did not provide any significant new information. They are given, together with further details on the near-IR spectra, in IMRI Internal Report No. 84-101-002.

In conclusion, the near-IR spectra of Narmco 5208 resin show distinct peaks which could be used to monitor the amount of unreacted epoxy and moisture in the resin.

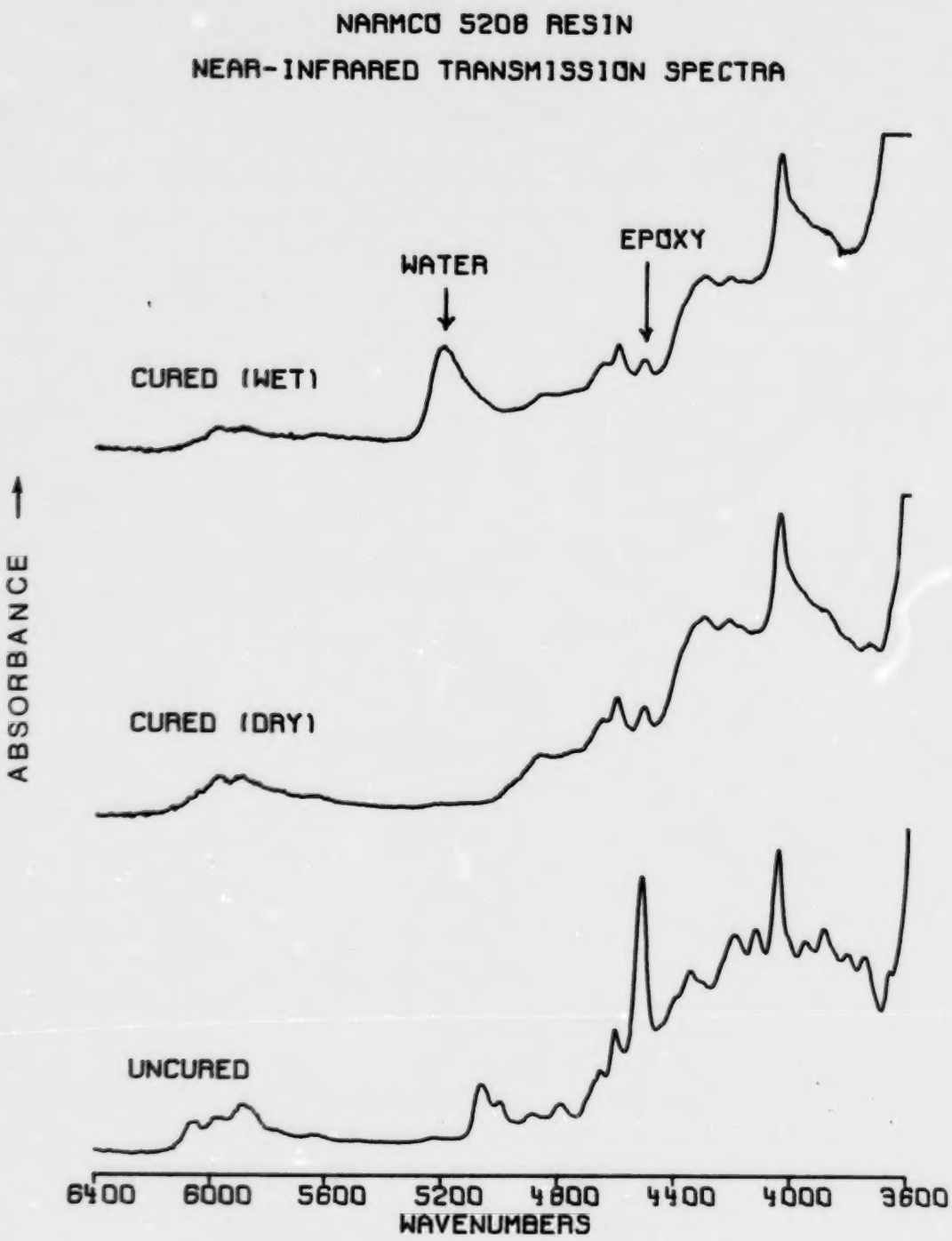


Figure 20 - Near-infrared transmission spectra of Narmco 5208 resin

3.8 Recommended Procedure for Quantitative Analysis of Narmco 5208 Prepreg by IR Transmission

(1) With clean scissors, and wearing gloves, cut a representative square of prepreg about 5 cm by 5 cm.

(2) With tweezers, carefully separate the prepreg from the plastic backing sheet and place it in a clean dry 250 mL Erlenmeyer flask.

(3) Add 25 mL of reagent grade acetone, stopper, and agitate gently for 15 minutes.

(4) Remove the graphite fibres with clean tweezers. The remaining solution contains about 25 mg/mL of resin.

(5) Prepare at least three (preferably five) clean windows of sodium chloride or potassium bromide. These should be of good quality with flat, highly polished surfaces. Repolish if necessary.

(6) In a location well protected from air currents, carefully deposit about 150 µL of resin solution in the centre of each window. A microsyringe can be used to control the amount. Stepwise addition is recommended to avoid having the solution flow over the edge. After each addition, let stand for a short time until the solvent evaporates. Do not blow with air and do not heat. Place the specimens under vacuum (without heating) for 15-30 minutes to remove residual solvent.

(7) Measure the infrared transmission spectra and convert to absorbance units. The strongest peak (1517 cm^{-1}) should have a maximum absorbance between 0.2 and 1.0, and there should be no obvious water vapour peaks in this region. If there are, they should be eliminated either by subtracting a reference spectrum of water vapour or by repeating the spectrum.

(8) Visually compare the spectrum with a reference spectrum of a typical batch and check for any unusual features.

(9) Calculate the areas of the peaks of interest using the available software with baselines drawn between the appropriate valleys. The following limits are suggested but

may be modified if necessary:

Aromatic ring (reference)	1545 - 1485 cm^{-1}
Single sulphone	1166 - 1119 cm^{-1}
Multiple sulphone	1166 - 1046 cm^{-1}
Single epoxy	923 - 875 cm^{-1}
Multiple epoxy	992 - 875 cm^{-1}
Epoxy + aromatic	874 - 779 cm^{-1}.

(10) Calculate "indices" by dividing the peak areas by the area of the aromatic ring reference peak. For routine analyses, the following two indices are considered sufficient: "multiple sulphone" and "multiple epoxy".

(11) The indices obtained for different specimens of the same prepreg sample should normally agree within about 2%. Specimens whose thickness is not uniform will give artificially high values. Specimens which give an index more than 5% higher than the lowest value should be rejected and repeated if necessary in order to give at least three good results for averaging.

(12) Compare the average values to the specifications to determine whether the batch is acceptable.

(13) Clean windows, syringes, etc. with acetone or a 50:50 mixture of acetone and toluene as soon as possible after use.

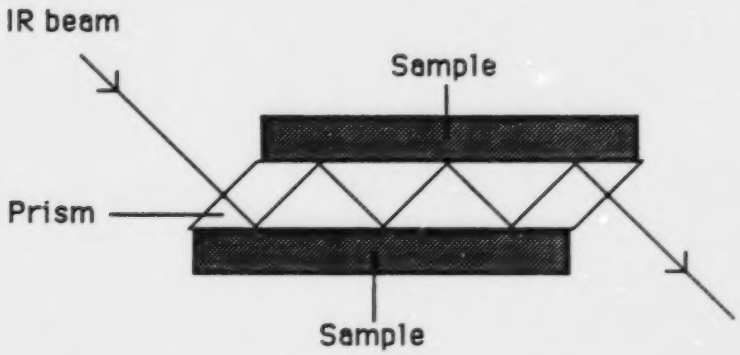
Note:

This method is suitable for typical B-stage resin. For more advanced prepreg, where the resin is less soluble, it is recommended to do a three-stage extraction using 50, 30, and 20 mL of acetone, followed by concentration of the combined extracts to a volume of about 25 mL on a rotary evaporator. A cloudy solution indicates a high degree of advancement and the results may be unreliable.

4. THE INTERNAL REFLECTION METHOD

4.1 Description of the Method

The technique of internal reflection spectroscopy, also known as attenuated total reflection (ATR) and multiple internal reflection (MIR), has been described in depth by Harrick [38]. A shorter description of the theory, together with some polymer applications, has been given by Knutson and Lyman [39]. The method is widely used for studying the surface of solid samples, and is also being used more and more for highly absorbing liquids and for "on-line" measurement in industrial processes. The principle is illustrated in the following diagram:

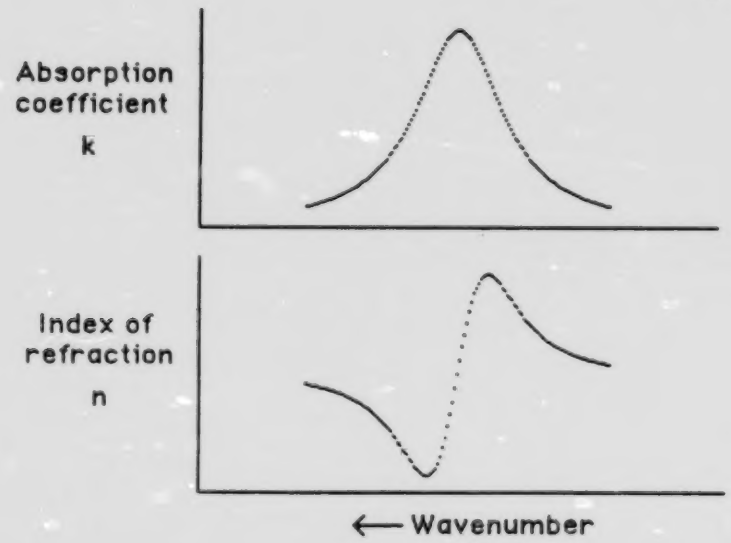


The sample is placed in intimate contact (using pressure if necessary) with an infrared-transmitting prism whose index of refraction is higher than that of the sample. Commonly used prism materials are KRS-5 (thallium bromoiodide) and germanium. In order for total internal reflection to occur, the geometry must be such that the angle of incidence is greater than a certain critical angle given by:

$$\sin \theta_c = n_s/n_p$$

where n_s and n_p are the refractive indices of the sample and prism respectively. Prisms with an angle of incidence of 45° or 60° are generally used. When an absorbing sample is in contact with the prism, the IR beam is "attenuated" by a partial absorption of the evanescent wave existing at the prism/sample interface. Before applying the sample to the prism, a "background" spectrum is recorded for the prism alone. The spectrum is then

measured with the sample present and ratioed against this background to give the spectrum of the sample. The exact nature of this spectrum depends on a number of factors such as angle of incidence, indices of refraction of both prism and sample, number of reflections occurring in the prism, and degree of contact between sample and prism. As a result, there are two important differences between ATR and transmission spectra. Firstly, whereas the transmission spectrum of a sample is determined almost exclusively by the absorption coefficient k (Section 3.4), in ATR the index of refraction n can also play an important role. Like k, n also varies with the frequency of the radiation, but in a different manner, as shown qualitatively in the diagram below. The absorption coefficient k is zero except in the vicinity of an absorption band, which usually has a Lorentzian shape. The refractive index n, on the other hand, is approximately constant at frequencies where there is no absorption, but when there is absorption it shows a dispersion-type variation. In ATR, the reflectance at the prism-sample interface is determined by the optical constants (n and k) of both the prism and the sample, as well as by the angle of incidence and the polarisation of the radiation. The exact relationship, which is rather complicated, is given by Fresnel's equations [38]. Generally speaking, when the angle of incidence is much larger than the critical angle, the refractive index contribution is negligible and the ATR spectrum resembles a transmission spectrum. If the angle of incidence is near the critical angle, the refractive index contribution becomes more important and "distorts" the spectrum by introducing some dispersion (derivative) character into the usual Lorentzian-type peak. Refractive index effects can therefore be minimized either by increasing the angle of incidence or by decreasing the critical angle (for example, by using a prism of higher refractive index).



The second difference between ATR and transmission spectra is that, even if refractive index effects are negligible, in ATR the effective sample penetration depth is proportional to the IR wavelength. As a result, ATR spectra appear "skewed" when compared to transmission spectra, with peaks at shorter wavelength (higher wavenumber) appearing less intense. This can be corrected mathematically. Under typical conditions, the effective penetration depth, as defined by Harrick [38], is of the order of magnitude of one micrometre.

4.2 The ATR Spectrum of Narmco 5208 Prepreg

The ATR method is particularly interesting for prepreg analysis because it is possible to measure the IR spectrum directly from the prepreg, without performing the solvent extraction step needed for transmission analysis. The prepreg is simply cut with scissors to give two strips of the appropriate size (about 5 x 1 cm), which are placed in contact with the prism in the ATR accessory. Finger pressure is usually sufficient to give good enough contact to obtain a suitable spectrum of the layer of resin on the surface. Unfortunately, cured composites are difficult to measure in this way because in order to achieve good contact, considerable pressure must be applied, and this can ruin the prism. Some work has been done on cured material [17, 40], but it required the preparation of samples with a very flat surface.

Figure 21 shows the ATR spectrum recorded for a sample of Narmco 5208/WC3000 prepreg (Batch 1010) using a 45° KRS-5 prism (single pass parallelogram, 50 x 10 x 3 mm). Comparison with the transmission spectrum of Figure 3 shows the two to be very similar but not identical. Firstly, the ATR spectrum shows a small peak at 1708 cm^{-1} which does not appear in the transmission spectrum. This was found to be due to a volatile product which was identified from its IR spectrum as acetone, apparently residual solvent from the prepreg manufacturing process. It is not seen in transmission because acetone is used to extract the resin from the prepreg and is then evaporated, together with any other volatiles present, before the spectrum is recorded. Secondly, the ATR spectrum shows an underlying background absorption, particularly at lower wavenumbers, which is due to the graphite fibres. The effect is more pronounced at low wavenumber because this corresponds to longer wavelength. The beam penetrates the surface layer of resin to a greater depth and is absorbed to a greater extent by the graphite cloth, which absorbs at all frequencies without distinctive peaks, as shown by the ATR spectrum of Figure 22. The importance of the graphite absorption will vary depending on the thickness of the surface layer of resin.

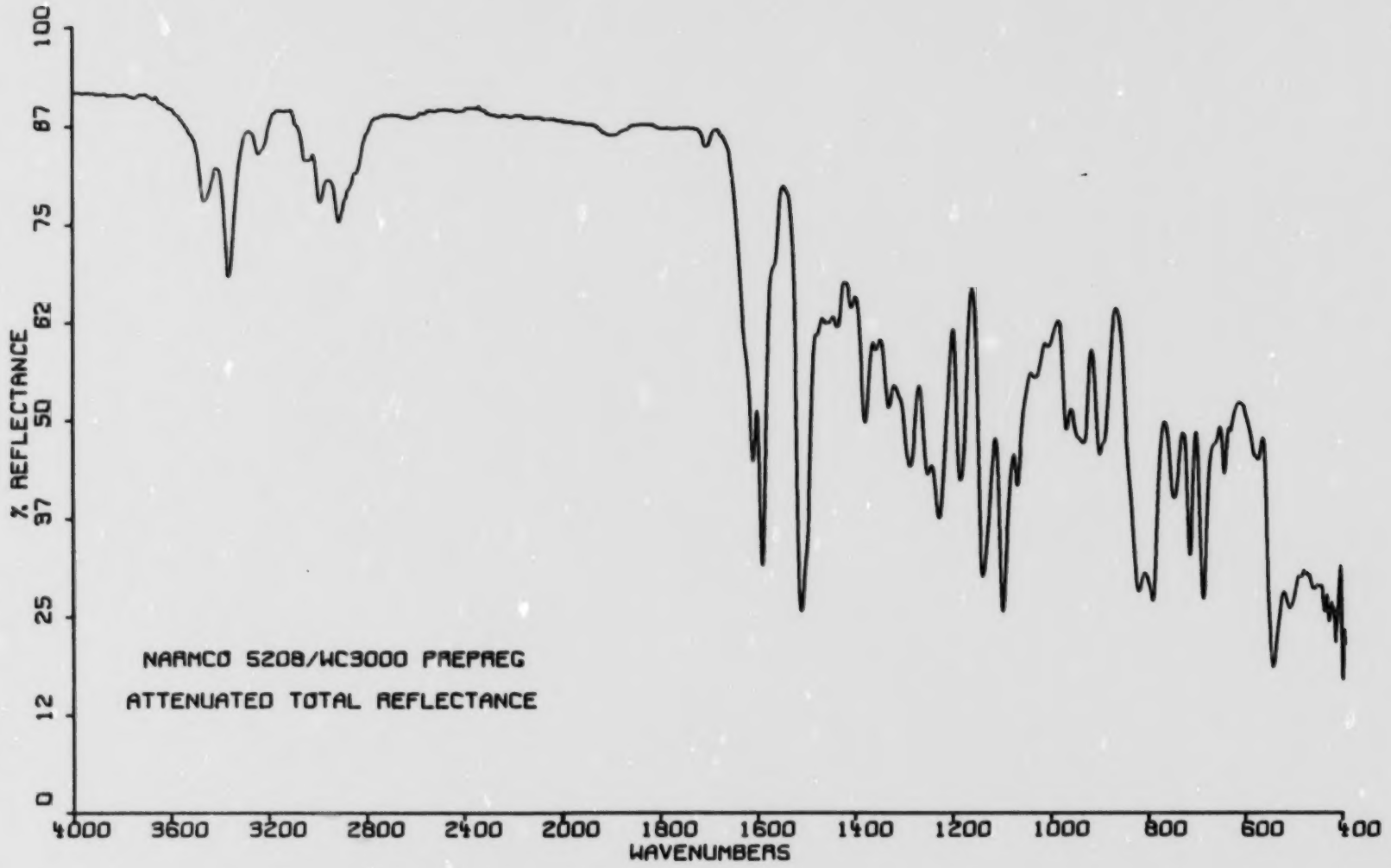


Figure 21 - Attenuated total reflectance IR spectrum of Narmco 5208/WC3000 prepreg Batch 1010 recorded using KRS-5 45° prism.

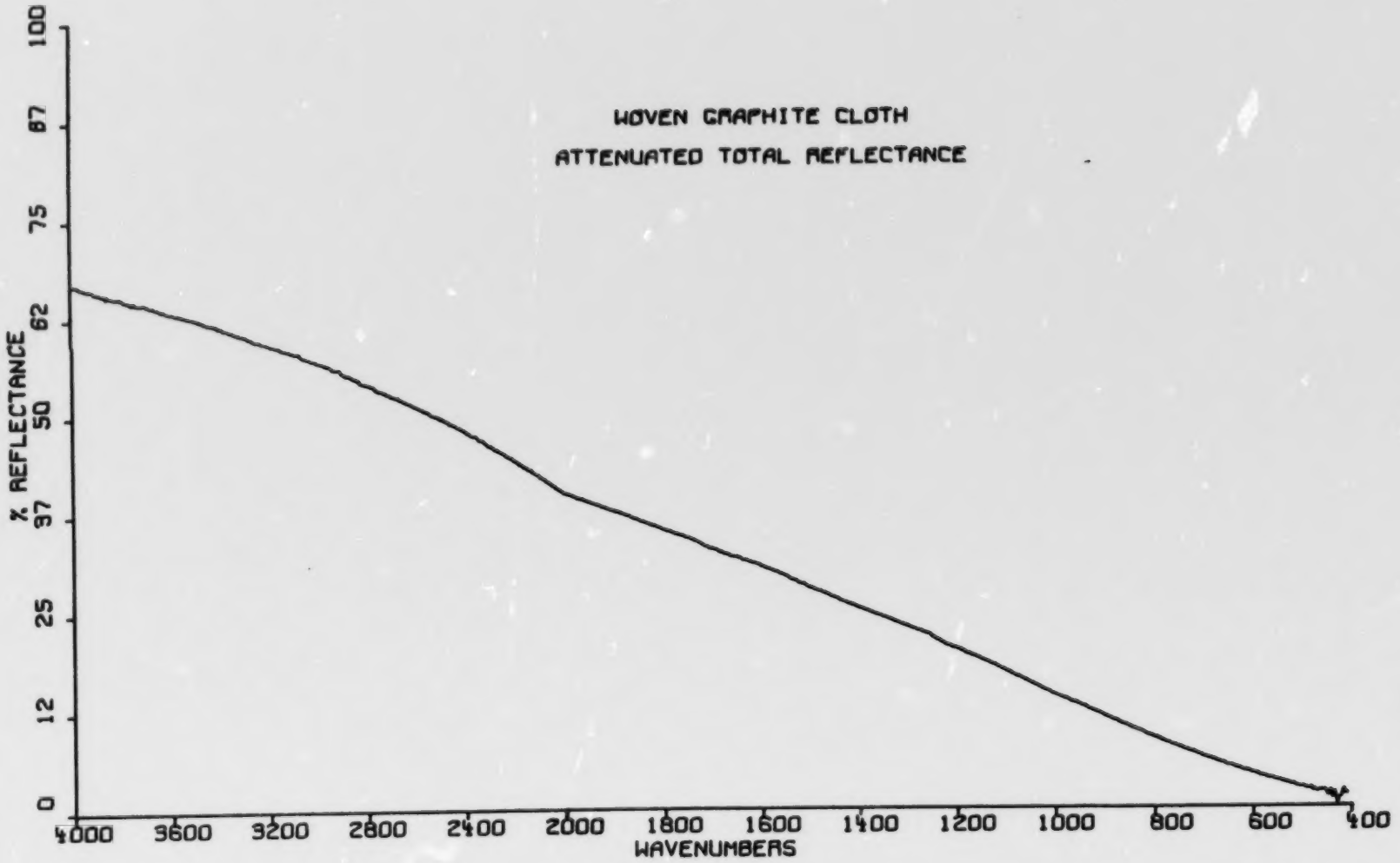


Figure 22 - Attenuated total reflectance IR spectrum of woven graphite cloth (KRS-5 prism, 45°)

The ATR spectrum can be better compared to the transmission spectrum if it is suitably transformed, as shown in Figure 23. This was done by converting to absorbance units, correcting the baseline, and then "normalizing" by multiplying by $\overline{\nu}/1000$, where $\overline{\nu}$ is the frequency in wavenumbers. The latter step corrects to a large extent for the variation of penetration depth with wavelength. However, when the resulting spectrum is compared to the absorbance spectrum measured in transmission (Figure 4) certain differences are still apparent in the form of variations in band shape which result in slight shifts of the peak maxima. These are most obvious in the case of the stronger peaks such as the aromatic ring band at 1517 cm^{-1}, the sulphone bands at 1146 and 1105 cm^{-1}, the aromatic/epoxy peak at 830 cm^{-1}, and the peak at 554 cm^{-1}. (The quoted frequencies correspond to the transmission spectrum of Figure 4.) The reason for this lies in refractive index effects. In regions of strong absorption, the refractive index of the resin increases and becomes closer to that of the prism. The critical angle, which is related to the difference in refractive index, increases and approaches the angle of incidence, with the result that the refractive index has a greater effect on the spectrum.

These effects can be reduced by using a larger angle of incidence or a prism of higher refractive index. This was checked by running ATR spectra using two other prisms, one of KRS-5 (n = 2.37) with an angle of 60°, and one of germanium (n = 4.0) with an angle of 45°. In Figure 24 these are compared (after the appropriate transformation) with the spectra just described. The KRS-5 60° prism gives some improvement over the KRS-5 45° one, but it is the Ge 45° prism which gives the spectrum most closely resembling the transmission spectrum. The differences are best seen by looking at the band near 830 cm^{-1}. One disadvantage of the Ge prism is that the spectrum ends at 700 cm^{-1} because Ge absorbs strongly beyond this point. A possible advantage of Ge is that the penetration depth is about four times lower than with KRS-5, so the effects of the graphite are less apparent.

4.3 Quantitative Analysis by ATR

A set of experiments was performed to investigate the feasibility of using the ATR method for quantitative analysis of the prepreg. The effects of several parameters were studied, namely:

(i) The type of prism. Three different prisms were used: KRS-5 (45°), KRS-5 (60°), and Ge (45°).

(ii) The presence or absence of prepreg. Spectra were recorded both with the

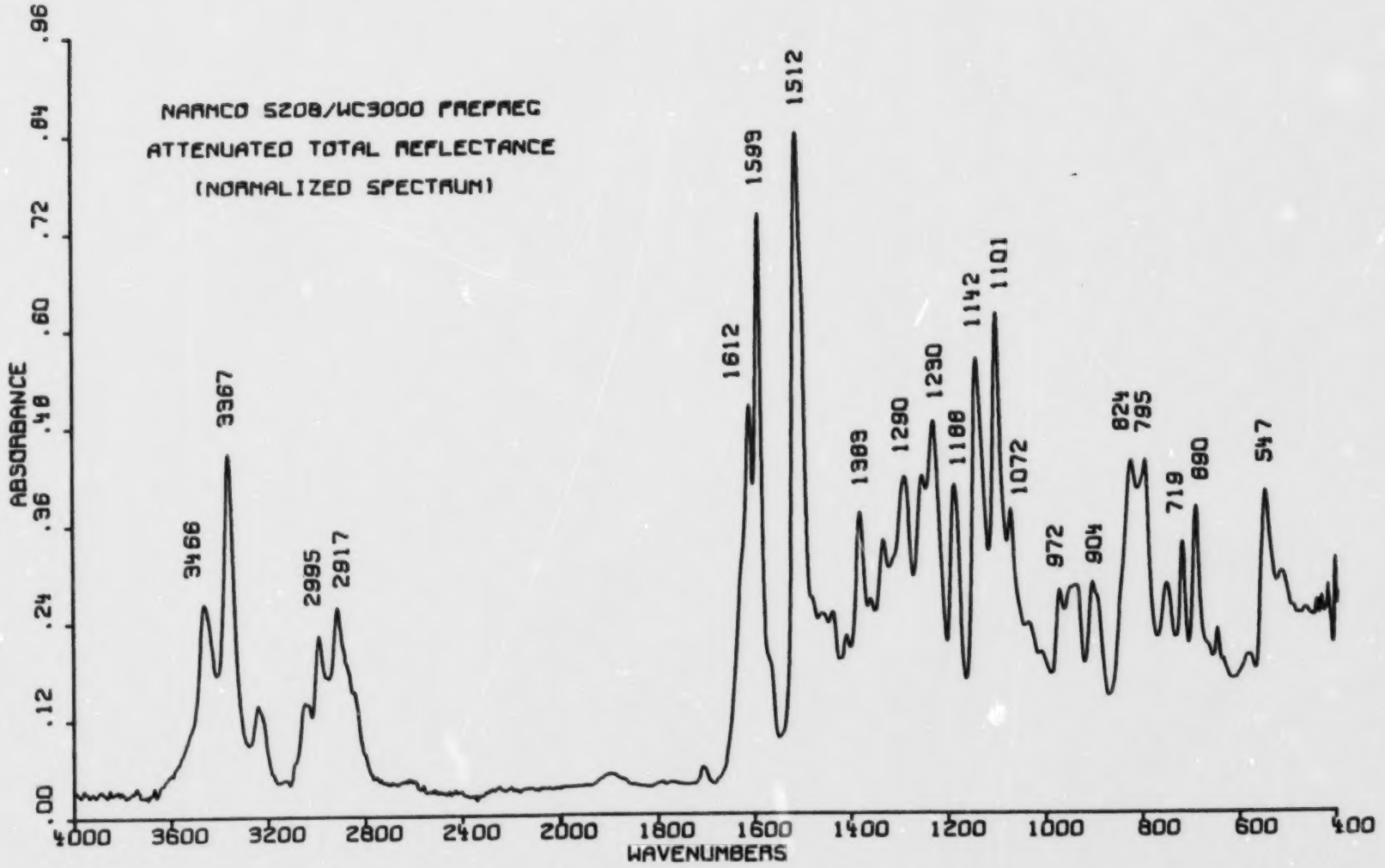


Figure 23 - ATR spectrum of Narmco 5208/WC3000 prepreg, after baseline correction and normalization.

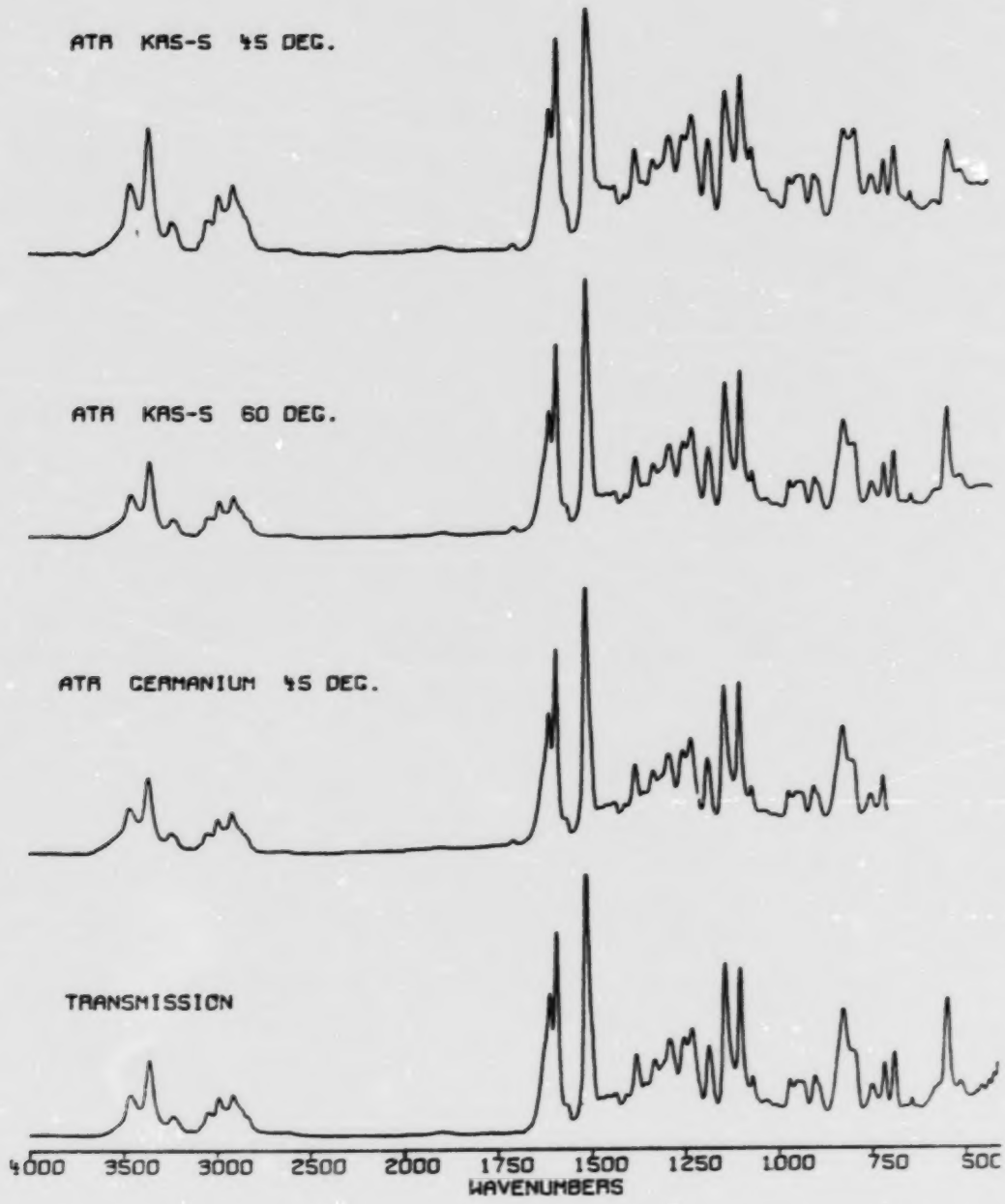


Figure 24 - Comparison of transmission and normalized ATR spectra of Narmo 5208 resin.

prepreg in contact with the prism and after removal of the prepreg. Sufficient resin is left behind on the prism to allow recording of the spectrum without interference from the graphite fibres. The two types of spectrum are labelled "prepreg" and "residue" respectively.

(iii) The fibre orientation. As a result of the 8-harness satin weave pattern used for the graphite cloth, on any given prepreg surface seven-eighths of the fibres are aligned in one direction (labelled the "principal fibre direction") while one-eighth are aligned in a direction perpendicular to this. (This is illustrated in Section 5.3.) Spectra were recorded with the principal fibre direction both parallel to the length of the prism and perpendicular to it.

Batch number 1010 of the Narmco 5208/WC3000 prepreg was selected for study. For each particular set of circumstances, five spectra were measured using fresh specimens for each spectrum. The prism was cleaned with solvent (50:50 acetone/toluene) after each specimen. The spectra were converted to absorbance and treated in the same way as the transmission spectra (Section 3.4). They were <u>not</u> normalized by multiplying by $\bar{\nu}/1000$ since this is an extra step which would not contribute anything to the results. It is necessary only when the spectra are to be directly compared with transmission spectra. When the calculated peak area ratios were examined, the fibre orientation was found to have no observable effect, so the figures for different orientations were combined, giving a total of ten results for averaging. These averages and their standard deviations (both absolute and relative) are shown in Table 6. Spectra measured for the case of the 45° KRS-5 prism with prepreg were not analysed because some bands were overly intense, due to the high effective penetration depth occurring under these circumstances. Examination of the results leads to the following comments:

(1) The reproducibility of the results appears to be lower in the case of the 45° KRS-5 prism, probably due to the greater "distortion" of peaks by refractive index effects, as discussed in Section 4.2. This would also explain why the ratios obtained with this prism are substantially different from those obtained with the others.

(2) The ratios obtained with "residue" spectra are somewhat lower than those obtained with "prepreg" spectra on the same prism. Since the precision is similar in both cases, and the "residue" spectra are not affected by graphite absorption, it might be expected that the "residue" spectra would be preferred. However, this is not the case, as there is another factor which must be considered, namely the thickness of the layer of residue. As pointed out previously, the beam penetration into the sample is proportional to wavelength (inversely proportional to wavenumber). If the layer of resin is sufficiently thin, the beam penetration may exceed the layer thickness at lower wavenumbers, causing

an apparent decrease in absorption intensity. This is the most probable explanation for the deviations observed in the present case. Because the sulphone and epoxy peaks occur at lower wavenumber than the aromatic reference band, they are more affected and the ratio with respect to the aromatic peak is lower than it is in the case of the "prepreg" spectra, where the effective resin layer is much thicker. The fact that the deviation is greater for the epoxy peaks than for the sulphone peaks offers further evidence, since the epoxy peaks occur at lower wavenumber. In the present case, the good reproducibility observed for the "residue" spectra indicates that the thickness of the residual layer is reasonably reproducible. However, a different batch of prepreg, with more viscous (more advanced) resin might leave a much thinner layer. To avoid possible problems related to such variation, it is recommended to record the spectra with the prepreg present.

Table 6. Quantitative analysis of Narmco 5208/WC3000 prepreg Batch 1010 by attenuated total reflection IR

Conditions	Index = Band area divided by area of aromatic reference band			
	Single sulphone	Multiple sulphone	Single epoxy	Multiple epoxy
KRS-5 (45°) Residue	0.595 (0.005, 0.9%)	1.836 (0.035, 1.9%)	0.311 (0.012, 4.0%)	0.938 (0.037, 4.0%)
KRS-5 (60°) Residue	0.562 (0.003, 0.5%)	1.523 (0.008, 0.6%)	0.234 (0.002, 0.9%)	0.698 (0.006, 0.8%)
KRS-5 (60°) Prepreg	0.573 (0.002, 0.3%)	1.561 (0.007, 0.4%)	0.246 (0.002, 0.8%)	0.729 (0.006, 0.8%)
Ge (45°) Residue	0.543 (0.003, 0.5%)	1.403 (0.006, 0.5%)	0.209 (0.002, 1.0%)	0.636 (0.008, 1.2%)
Ge (45°) Prepreg	0.554 (0.001, 0.2%)	1.436 (0.007, 0.5%)	0.220 (0.003, 1.3%)	0.669 (0.008, 1.2%)

(3) Although there is not a lot of difference between the KRS-5 (60°) and Ge (45°) results, the Ge (45°) prism is preferred since refractive index effects are less important and the spectrum better resembles the transmission spectrum. The ratios given in Table 6 are considerably different from those obtained in transmission (Table 3) because the ATR spectra were not normalized. However, the results can be compared if the ATR indices are "corrected" for beam penetration effects by multiplying by $\bar{\nu}$(peak)/$\bar{\nu}$(reference), where $\bar{\nu}$(peak) is the wavenumber corresponding to the centre of the peaks in question, and $\bar{\nu}$(reference) is the wavenumber of the aromatic reference peak. This gives the results shown in Table 7. The ATR ratios are now very close to those obtained in transmission.

Table 7. Comparison of IR transmission and ATR results for Narmco 5208/WC3000 prepreg Batch 1010

Conditions	Index = Band area divided by area of aromatic reference band			
	Single sulphone	Multiple sulphone	Single epoxy	Multiple epoxy
Ge (45°) Prepreg Normalized	0.418	1.065	0.131	0.410
Transmission	0.428	1.072	0.131	0.402

In view of the results just described, the ATR method is recommended over the transmission method for the quantitative analysis of uncured prepreg based on epoxy resins and graphite fibres. Not only is sample preparation faster and simpler, but the results are just as reproducible, if not more, since the problem of variation in sample thickness associated with the transmission method is avoided. A further advantage of the ATR method is that it gives the spectrum of the prepreg as received, whereas the transmission method requires more extensive sample preparation which can change the resin composition. Thus ATR can detect volatile materials such as acetone, which are not detected by the transmission method (Section 4.2).

A detailed description of the recommended ATR method is given in Section 4.5.

4.4 Comparison of Different Batches

Six of the seven batches of Narmco 5208 analysed by IR transmission (Section 3.5) were also analysed by the recommended ATR method. Batch Number 1023 was excluded because it consisted of neat resin rather than prepreg. The results are summarized in Table 8. Each result is an average over five specimens with the standard deviation shown in parentheses. In most cases the deviation is less than 1%, so the reproducibility appears to be as good as in transmission. The calculated indices differ from those obtained in transmission because they are not corrected for the frequency dependence of the sample penetration. As in transmission, comparison of the different batches shows no substantial variations. All multiple sulphone ratios lie within ±2% of the mean (1.481), and all multiple epoxy ratios lie within ±3% of the mean (0.677). These ranges are only about half as wide as observed in transmission, and the reason is not obvious. However, the general trends are much the same. Using the multiple epoxy index, the batches can be arranged in order of free epoxy content as follows: 1047 > 1101 > 1014 ≈ 1010 > 1104 > 1103. Except for 1101 and 1014, this is the same order found by transmission. The sulphone results are more difficult to interpret, as was the case in transmission, because of the low overall variation. About the only reasonably definite conclusion which can be drawn, based on the multiple sulphone indices observed in ATR and transmission, is that BN 1101 appears to have a slightly low hardener content.

Table 8. Quantitative analysis of different batches of Narmco 5208/WC3000 prepreg by attenuated total reflection IR

Batch No.	Index = Band area divided by area of aromatic reference band			
	Single sulphone	Multiple sulphone	Single epoxy	Multiple epoxy
1010	0.558 (0.002)	1.482 (0.006)	0.231 (0.002)	0.677 (0.008)
1014	0.552 (0.003)	1.486 (0.009)	0.234 (0.002)	0.676 (0.006)
1101	0.565 (0.002)	1.457 (0.005)	0.239 (0.002)	0.688 (0.004)
1103	0.582 (0.001)	1.509 (0.004)	0.228 (0.001)	0.656 (0.005)
1104	0.565 (0.005)	1.468 (0.012)	0.230 (0.004)	0.668 (0.015)
1047	0.568 (0.001)	1.484 (0.002)	0.237 (0.001)	0.694 (0.003)

4.5 Recommended Procedure for Quantitative Analysis of Narmco 5208 Prepreg by IR Spectroscopy Using ATR

(1) Make sure that the internal reflection accessory is installed in the spectrometer and properly aligned. A 45° germanium prism of length 50 mm is recommended.

(2) With clean scissors, and wearing gloves, cut two strips of prepreg of approximately the same size as the prism surface.

(3) Record the "background" spectrum using the clean prism only, accumulating as many scans as necessary to give an acceptable noise level (at least 100).

(4) With tweezers, carefully remove the plastic backing sheet from the prepreg samples and place the freshly exposed surfaces in contact with the prism, one on each side. Press with the fingers to ensure good contact. If the prepreg has lost its tack and flexibility, it may be necessary to use pressure clamps to achieve sufficient contact.

(5) Record the spectrum with the prepreg in place and ratio against the background spectrum.

(6) Convert the spectrum to absorbance and check the intensity. The strongest peak (1517 cm^{-1}) should have a maximum absorbance between 0.2 and 1.0, and there should be no obvious water vapour peaks in this region. If there are, they should be eliminated either by subtracting a reference spectrum of water vapour or by repeating the spectrum.

(7) Visually compare the spectrum with a reference spectrum of a typical batch and check for any unusual features.

(8) Calculate the areas of the peaks of interest using the available software with baselines drawn between the appropriate valleys. The following limits are suggested but may be modified if necessary:

Aromatic ring (reference)	1545 - 1485 cm^{-1}
Single sulphone	1163 - 1120 cm^{-1}
Multiple sulphone	1163 - 1043 cm^{-1}

Single epoxy	921 - 872 cm^{-1}
Multiple epoxy	992 - 872 cm^{-1}.

(9) Calculate "indices" by dividing the peak areas by the area of the aromatic ring reference peak. For routine analyses, the following two indices are considered sufficient: "multiple sulphone" and "multiple epoxy".

(10) Measure at least three different specimens of a given prepreg sample. The spread between the lowest and highest values of a given index should not exceed 5%. If so, more specimens should be measured in order to obtain at least three good results for averaging.

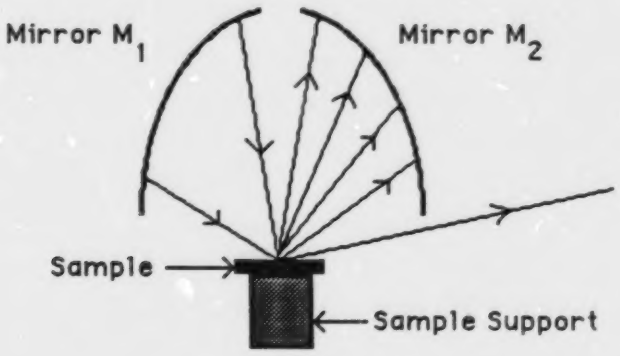
(11) Compare the average values to the specifications to determine whether the batch is acceptable.

(12) After each specimen, the prism should be cleaned with solvent (acetone or 50:50 acetone-toluene) and thoroughly dried. Cotton wool swabs are recommended for wiping the prism.

5. THE DIFFUSE REFLECTION METHOD

5.1 Description of the Method

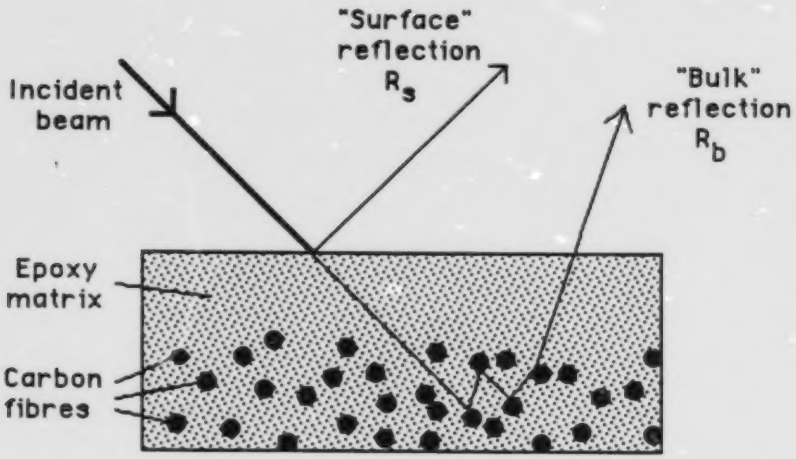
Although diffuse reflection (DR) spectroscopy has been known and studied for a long time, it did not come into widespread use in infrared spectroscopy until the highly sensitive FTIR instruments were developed. Since then it has proved extremely useful in a number of applications [41-44]. It is sometimes referred to as DRIFT (Diffuse Reflectance Infrared Fourier Transform). The following diagram illustrates the principle:



An elliptical mirror (M_1) focuses the infrared beam onto the surface of the sample, which may be a powder or a rough surface. Part of it is absorbed and the rest is reflected in all directions. A second elliptical mirror (M_2) captures some of this scattered (diffuse) radiation and focuses it toward the infrared detector for analysis. The resulting spectrum is compared to that of a non-absorbing reference such as powdered potassium bromide in order to determine the absorption properties of the sample.

Although generally applied to powders, diffuse reflection can be applied to any matte surface which reflects diffusely. As a result, it is particularly interesting for the study of composites, because it can be used not only for prepreg but also for cured parts. The spectrum can be obtained directly from the surface with no sample preparation other than cutting a piece small enough to fit inside the reflectance accessory. With certain types of accessory ("upward-looking" models) even this is not necessary, and actual parts can be examined in a non-destructive manner. Recently Young et al. [45, 46] have reported use of the method to study curing and degradation in composites.

Unfortunately, diffuse reflection suffers from one important complication, namely front-surface reflection [47]. This is illustrated below for the case of a fibre-reinforced epoxy-matrix composite.



When the incident infrared beam impinges on the sample surface, part of it is reflected immediately before it ever enters the sample ("surface" reflection R_s). This reflection is governed by the laws of Fresnel, and depends on the angle of incidence, the polarisation of the beam, the index of refraction n of the sample, and the absorption coefficient k. The general relationship is quite complex, but for the special case of normal incidence it reduces to:

$$R = \frac{(n-1)^2 + \left(\frac{k}{4\pi\bar{\nu}}\right)^2}{(n+1)^2 + \left(\frac{k}{4\pi\bar{\nu}}\right)^2}$$

where $\bar{\nu}$ is the frequency in wavenumbers. As discussed in Section 4.1, both k and n vary with frequency. In regions where there is no absorption ($k = 0$), n is approximately constant, and for a typical organic material ($n \approx 1.5$), R is of the order of 4%. In the region of an absorption band, k passes through a maximum while n varies according to a

dispersion-type curve. The net result is that the reflectivity varies with frequency and, paradoxically, can increase substantially at frequencies where the sample strongly absorbs. This is known as the reststrahlen effect. In the limiting case of very large k, R becomes equal to 1, or 100%.

That part of the beam which enters the sample undergoes absorption according to the Beer-Lambert law:

$$I = I_0 \exp(-kb)$$

where I_0 is the intensity of the entering beam, and I is the intensity after it has travelled a distance b within the sample. Eventually, it encounters a fibre-epoxy interface, where partial reflection occurs. After one or more such reflections, it can leave the sample again as R_b (for "bulk" reflection). The frequency dependence of this beam can be quite different from that of R_s because it depends primarily on k rather than on n. It more closely resembles that of a normal transmission spectrum. Both R_s and R_b are detected by the infrared detector, and the form of the resulting spectrum depends on the relative contributions of the two, which in turn depend on the nature of the sample. In some cases (for example, organic powders dispersed in KBr powder), R_s is negligible and the spectrum is similar to the transmission spectrum. In other cases (for example, highly absorbing materials or inorganic materials with a high index of refraction) R_s can dominate the spectrum to the point where it is almost unrecognizable compared to the transmission spectrum.

Even when front-surface reflection is negligible, the diffuse reflectance spectrum differs somewhat from the transmission spectrum, as a result of the physical differences involved. Absorption bands occur at much the same frequencies, but their relative intensities are different, since the Beer-Lambert law is not directly applicable. Instead, the following equation, which was developed by Kubelka and Munk, is widely used:

$$F(R_\infty) = (1 - R_\infty)^2 / 2R_\infty = k/s$$

In this equation, R_∞ is the diffuse reflectance of the sample, which is assumed to be "infinitely thick", k is the absorption coefficent, and s is a scattering coefficient. The equation may be compared with the Beer-Lambert law for transmission:

$$A = -\log_{10}T = 0.4343\,kb$$

where A is the absorbance, T is the transmittance, and b is the sample thickness. Both the Kubelka-Munk function $F(R_\infty)$ and the absorbance A are related to the absorption coefficient k, but whereas b is a constant, the scattering coefficient s varies with frequency. Usually, however, the variation is gradual, and a diffuse reflectance spectrum converted to Kubelka-Munk units is very similar, although not identical, to a transmission spectrum converted to absorbance units. Although the Kubelka-Munk equation was derived for the case of a powdered sample, it is sometimes applied to other types of sample for which an appropriate model is lacking.

5.2 The Diffuse Reflectance Spectrum of Narmco 5208 Prepreg

Figure 25 shows the diffuse reflectance spectrum, as measured, of Narmco 5208/WC3000 prepreg (Batch 1010). To obtain this spectrum, a small square of prepreg (about 1 cm x 1 cm) was cut with scissors and mounted with double-sided adhesive tape on a flat horizontal support whose height could be adjusted to optimize the energy throughput in the diffuse reflectance accessory. The support was obtained from Harrick Scientific Corp. and is normally supplied with a mirror for checking the performance of the DR accessory. The sample height adjustment was found to be quite critical. As discussed in the next section, fibre orientation was also found to be important; the spectrum shown was obtained using the optimum orientation. All diffuse reflectance spectra discussed in this report were measured using as a "background" powdered infrared-grade potassium bromide placed in the standard sampling cup (14 mm diameter) and compacted with a spatula to give a smooth level surface. Spectra were generally recorded using 128 scans.

The most striking feature of the spectrum is the strong background absorption, which prevents the overall reflectance from exceeding about 40%. This is due largely to absorption by the graphite fibres, and is more pronounced than in the ATR spectra because the beam penetrates further into the prepreg and interacts with the graphite to a greater extent. The DR spectrum of graphite cloth is shown in Figure 26; as in ATR (Figure 22), there are no distinctive peaks. In the ATR spectrum the reflectance decreases at lower wavenumber because the effective penetration depth, and hence the absorption, increases with wavelength. In the DR spectrum, this is not the case. Instead the reflectance decreases somewhat toward higher wavenumber, probably because of increased scattering losses, which affect the shorter wavelengths to a greater extent. All the peaks seen in

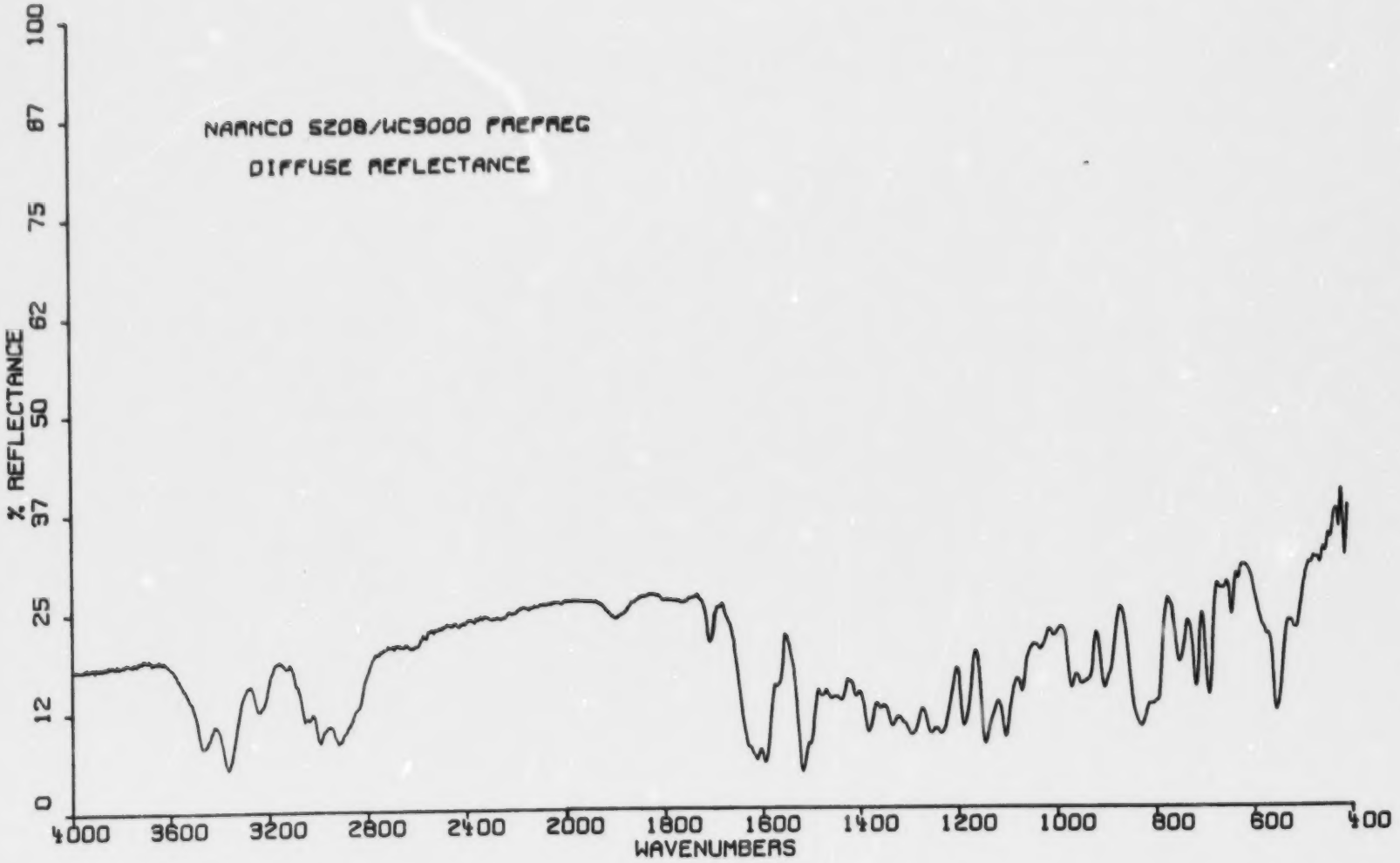


Figure 25 - Diffuse reflectance IR spectrum of Narmco 5208/WC3000 prepreg Batch 1010, as recorded.

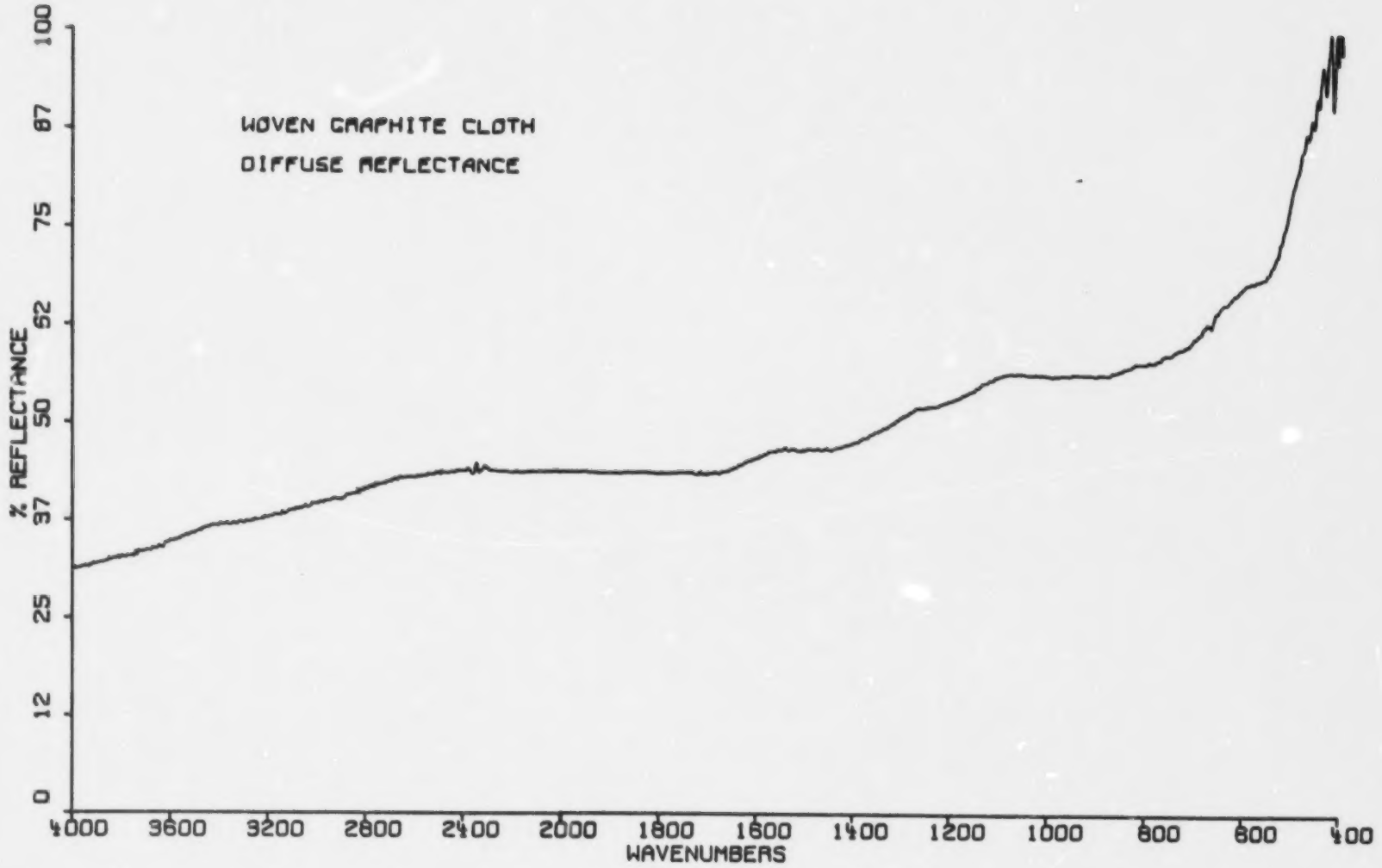


Figure 26 - Diffuse reflectance IR spectrum of woven graphite cloth.

Figure 25 correspond to those observed in transmission (Figure 3), except for the peak at 1708 cm^{-1}, which is due to residual acetone left in the prepreg by the solvent impregnation process. This peak is also observed in ATR (Section 4.2). Figure 27 shows the prepreg spectrum of Figure 25 after conversion to Kubelka-Munk units and correction of the baseline to remove the graphite absorption. When this is compared to the transmission spectrum in absorbance units (Figure 4), it is seen to be very similar, although there are slight differences in peak positions, band shape, and relative peak intensities. However, there is no loss of detail in the diffuse reflectance spectrum.

Figure 28 shows the DR spectrum of a cured test panel made from four plies of Narmco 5208/WC3000 prepreg (Batch 1014). This was measured in the same way as for the prepreg using a small square cut with a jigsaw and attached to the sample support using two-sided adhesive tape. As in the case of the prepreg, the graphite absorption is important, but when converted to Kubelka-Munk units and baseline-corrected, the spectrum (Figure 29) bears a close resemblance to the transmission spectrum (Figure 9). Since the test panel was cured under vacuum, there are no oxidation peaks at 1722 and 1667 cm^{-1}. The weak but definite peaks in the 1000-900 cm^{-1} region show that this particular panel contains a significant number of unreacted epoxy groups. This spectrum is of excellent quality and illustrates very well the usefulness of diffuse reflectance FTIR as a non-destructive method for monitoring the cure and composition of graphite-epoxy composites. (For the method to be truly non-destructive, it would be necessary to use a different sampling configuration which would not require cutting a piece of the sample.)

5.3 Importance of Fibre Orientation

As mentioned in Section 4.3, the prepreg used in this work involved graphite cloth based on an 8-harness satin weave pattern, which is illustrated in the diagram following this paragraph. Each fill yarn passes alternately over seven warp yarns and under one. Consequently, on a given prepreg surface, seven-eighths of the total area is covered by fibres aligned in one particular direction, which will be called the "principal fibre direction". To check the importance of sample orientation, spectra were measured for a given sample in the Harrick "praying mantis" accessory using two different orientations of the principal fibre direction with respect to the beam propagation direction of the instrument, i.e. "parallel" and "perpendicular". The results are shown in Figure 30. It is immediately obvious that the "parallel" orientation gives much better spectra, both for uncured prepreg and cured panels. The overall energy throughput is two to four times higher and the spectral contrast is much enhanced. All subsequent DR spectra were

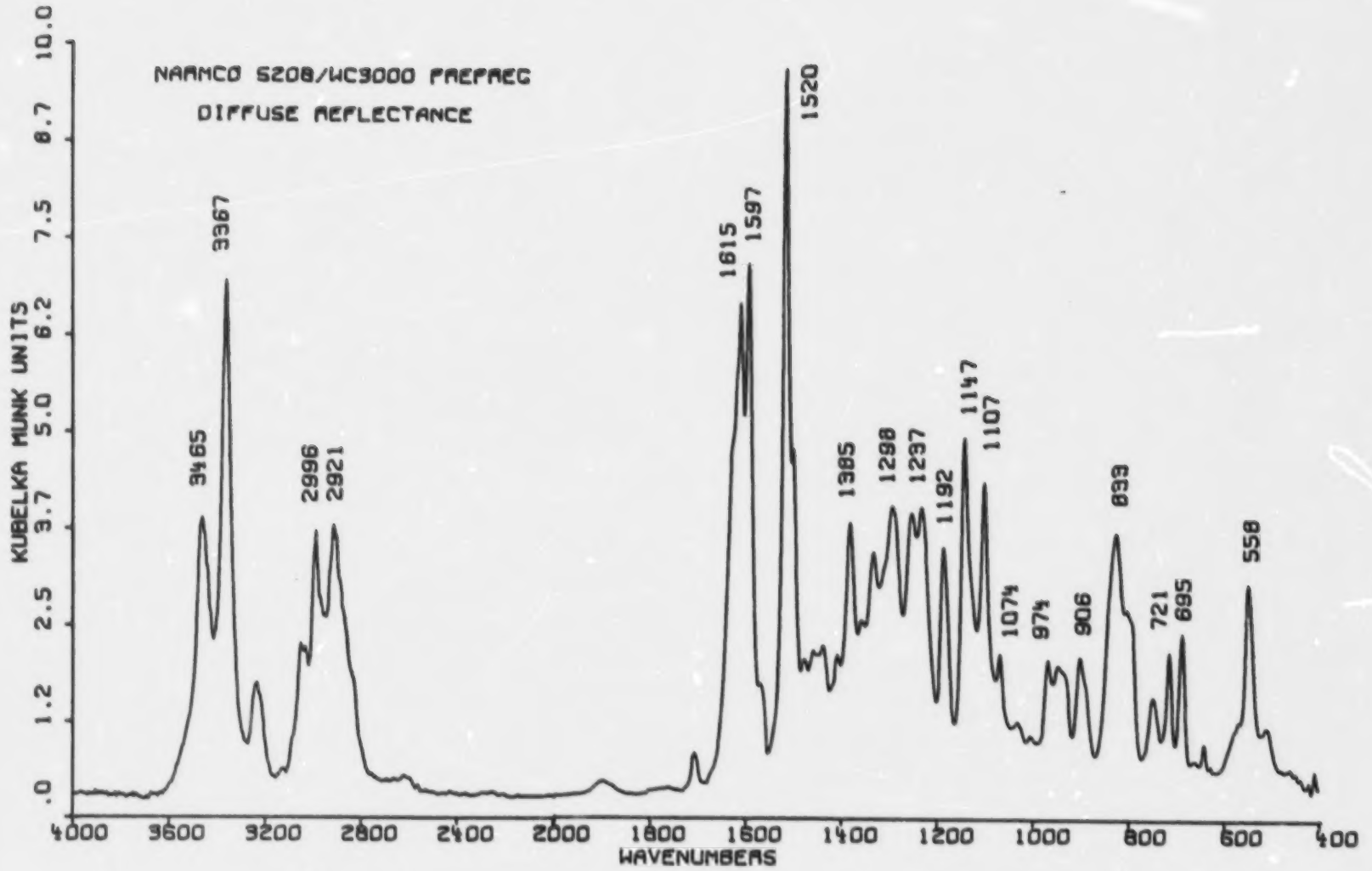


Figure 27 - Diffuse reflectance IR spectrum of Narmco 5208/WC3000 prepreg, after conversion to Kubelka-Munk units and baseline correction.

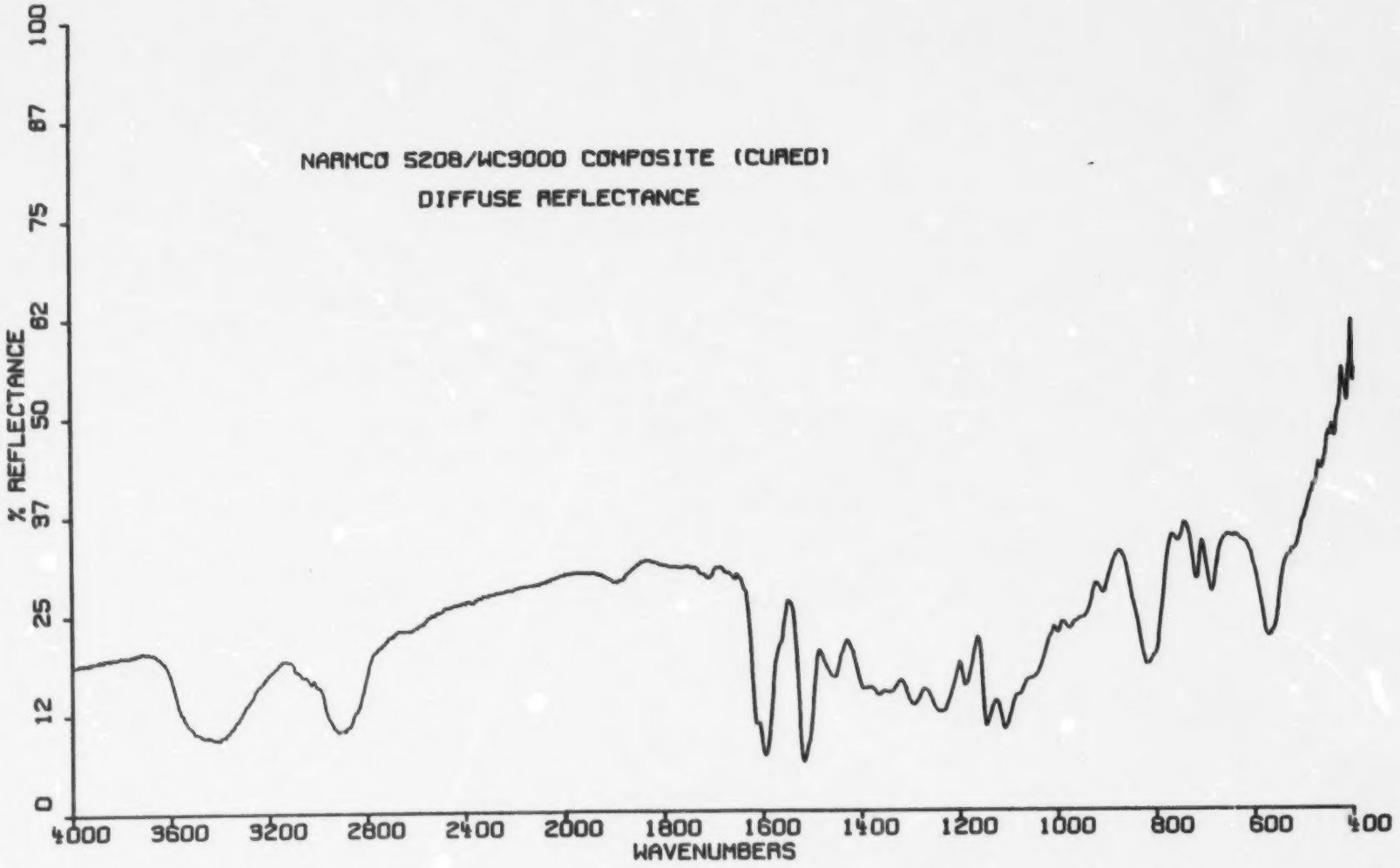


Figure 28 - Diffuse reflectance IR spectrum of cured laminate made from Narmco 5208/WC3000 prepreg.

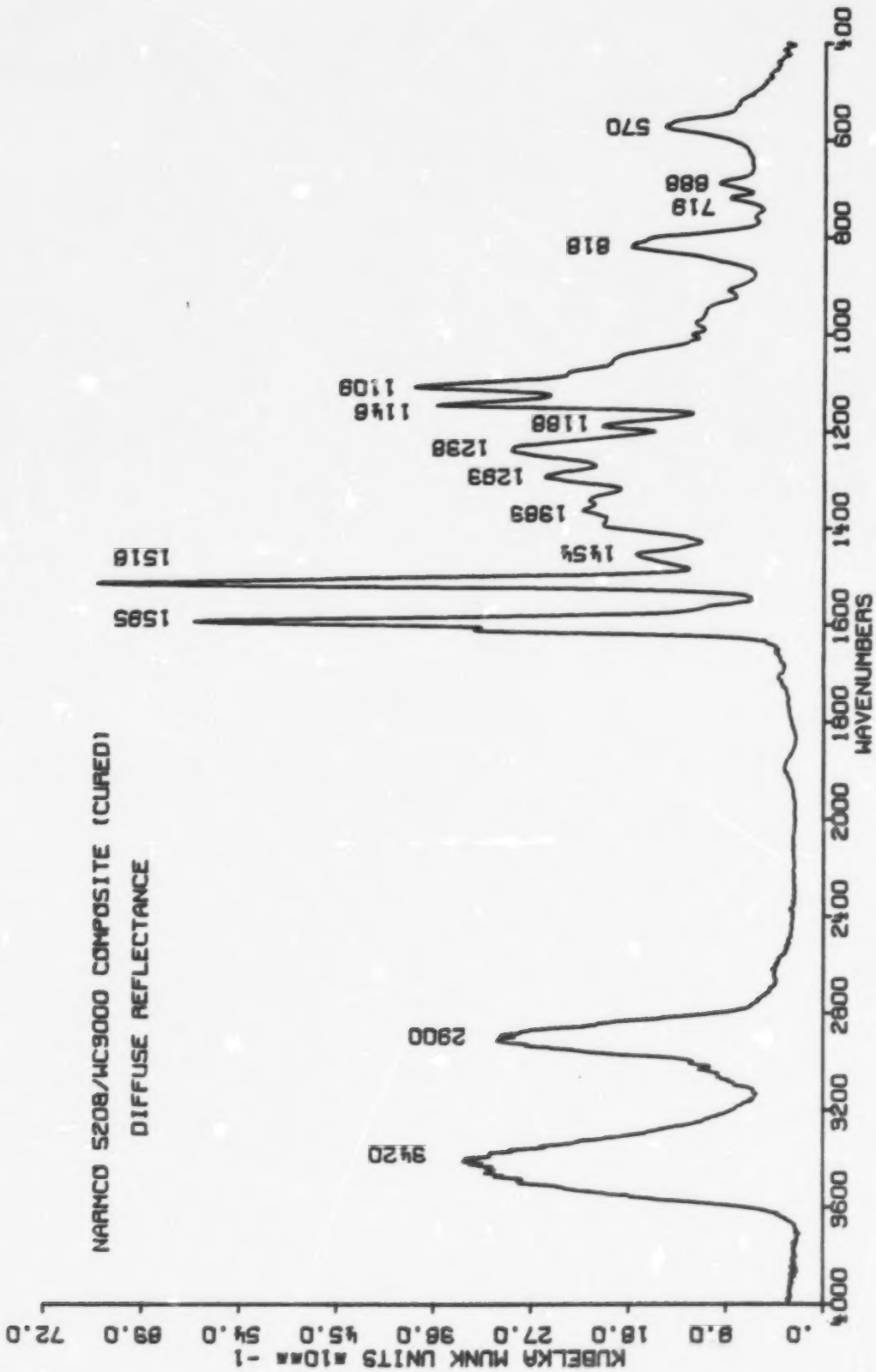


Figure 29 - Diffuse reflectance IR spectrum of cured laminate made from Narmco 5208/WC3000 prepreg, after conversion to Kubelka-Munk units and baseline correction.

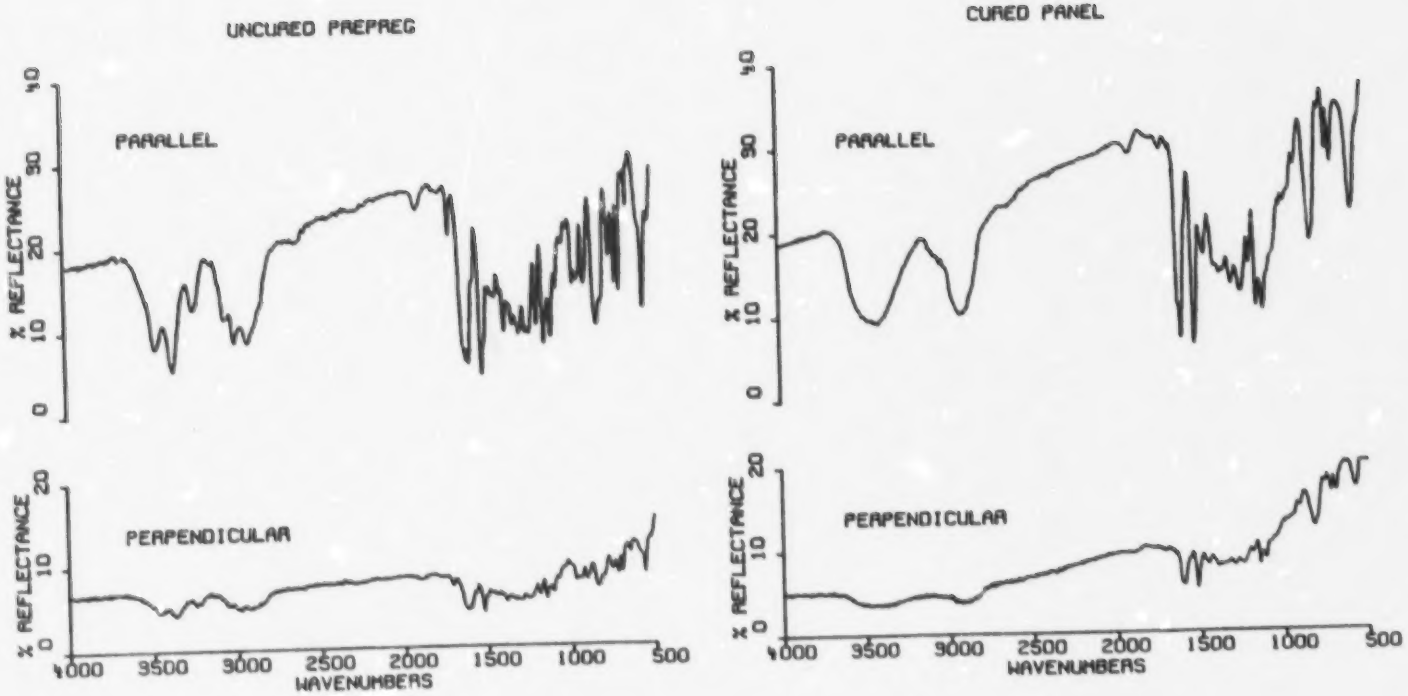
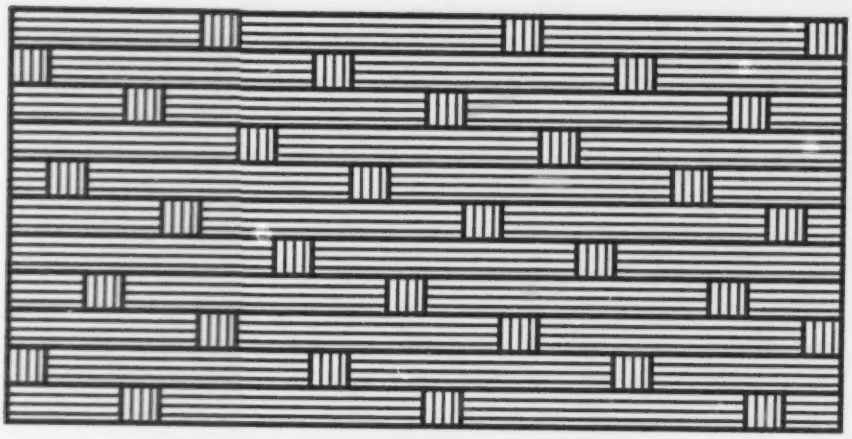


Figure 30 - Effect of fibre orientation direction on diffuse reflectance IR spectrum of Narmco 5208/WC3000 prepreg and cured laminate.

measured using the "parallel" orientation. This effect would be expected to be even more important for materials based on unidirectional tape, but would not be significant for those based on a regular two-dimensional weave pattern.



⟵ Principal fibre direction ⟶

8-harness satin weave pattern

5.4 Quantitative Analysis by Diffuse Reflection

As in the case of transmission and ATR, an experiment was done to evaluate the feasibility of using diffuse reflectance for quantitative analysis of the prepreg. Although there are complications associated with the technique, it was felt that these might be reproducible enough so that it could still be used, if only in a somewhat more empirical manner than the other methods. If so, it would offer two important advantages: negligible sample preparation and the fact that it can be applied to composites at all stages of cure.

The prepreg used was Narmco 5208/WC3000, Batch 1010. A total of eighteen specimens were cut and measured using the optimized procedure outlined in Section 5.7. Spectra were converted to both Kubelka-Munk and absorbance units and peak areas and ratios were calculated in the same way as for transmission and ATR. The results are summarized in Table 9. The reproducibility is unacceptably poor, with standard deviations up to 16%. The results obtained using absorbance units are somewhat more reproducible, even though conversion to absorbance is less "correct" and the spectra do not resemble the true absorbance spectra as well as those expressed in Kubelka-Munk units. Nevertheless,

the variation is still unacceptably high for routine quantitative analysis.

Table 9. Quantitative analysis of Narmco 5208/WC3000 prepreg Batch 1010 by diffuse reflection IR

Units used	Index = Band area divided by area of aromatic reference band			
	Single sulphone	Multiple sulphone	Single epoxy	Multiple epoxy
Kubelka-Munk units	0.408 (0.044, 10.8%)	1.118 (0.127, 11.4%)	0.179 (0.028, 15.6%)	0.567 (0.085, 15.0%)
Absorbance units	0.489 (0.028, 5.7%)	1.486 (0.097, 6.5%)	0.314 (0.029, 9.2%)	0.986 (0.088, 8.9%)

Close examination of the set of spectra obtained showed a variation in the shapes of certain bands. For instance, the aromatic ring reference band near 1520 cm^{-1} is particularly affected and the shoulder near 1500 cm^{-1} varies dramatically in prominence. The reason for this is believed to be primarily a variation of the thickness of the surface layer of resin on the prepreg, which gives rise to a variation in the relative importance of front-surface reflection effects. When the layer is thicker, the part of the beam which penetrates the resin is highly absorbed, so the component R_b is diminished and R_s dominates the spectrum. The effect is illustrated in Figure 31, which compares four different spectra of Narmco 5208. On the top left is the true transmission spectrum. On the top right is a true front-surface reflection spectrum, measured with a Harrick External Specular Reflection Attachment (30°) on a thick layer of 5208 resin deposited on a transparent KBr window. It is quite different from the transmission spectrum; the "dispersion-like" distortion caused by the refractive index variation is very evident. Below these spectra are two diffuse reflectance spectra measured on prepreg. One ("resin-poor") was measured for a specimen bearing a thin layer of resin on the surface. It resembles the transmission spectrum fairly well. The other ("resin-rich") was obtained for a specimen where the layer of resin was obviously thicker. Compared to the "resin-poor" spectrum, the band shapes are distorted and approach those of the front-surface reflection spectrum, thus confirming the postulated

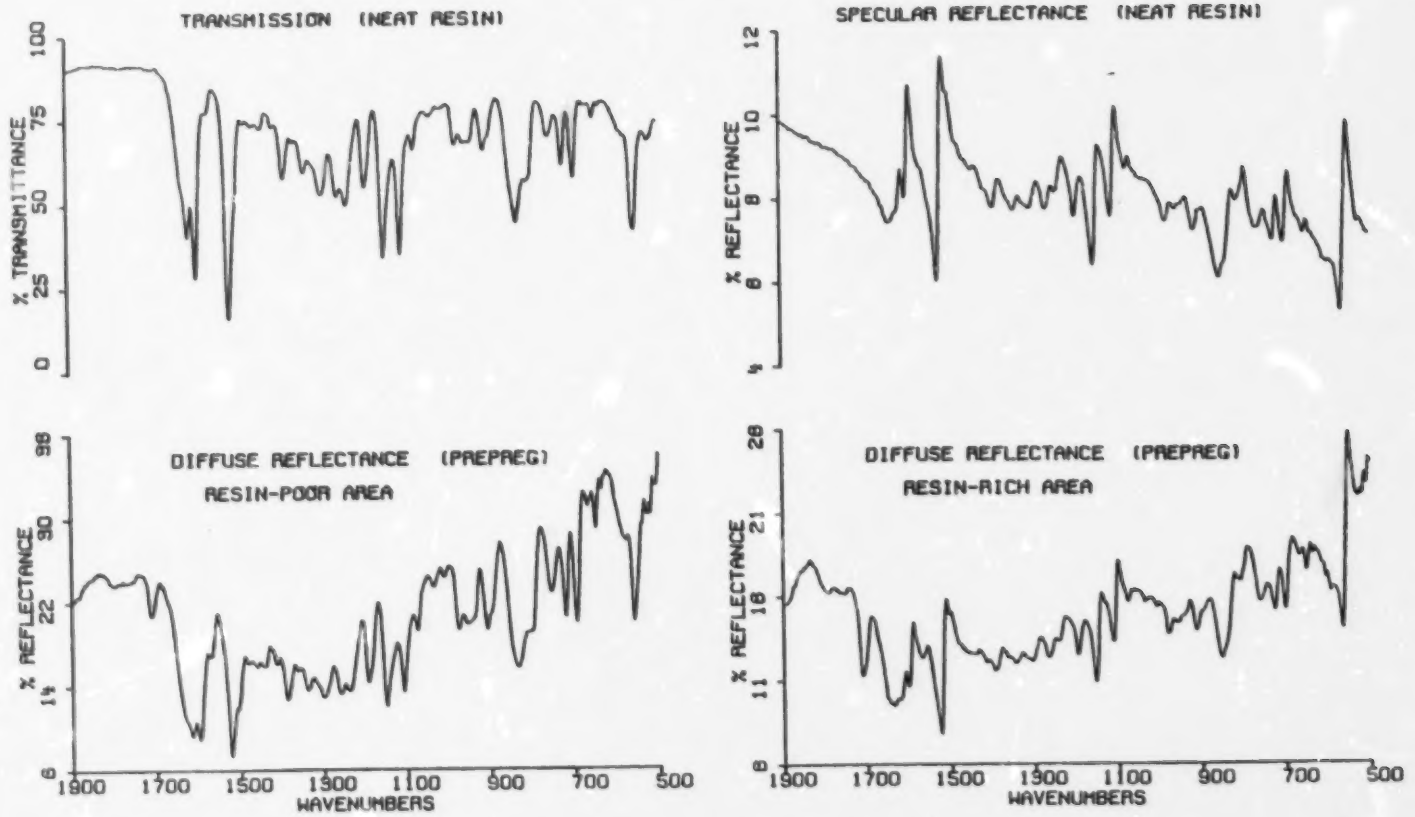


Figure 31 - Comparison of transmission, specular reflectance, and diffuse reflectance IR spectra of Narmco 5208 resin and prepreg.

reason for the variation in the diffuse reflectance spectra.

It has been demonstrated [48-50] that the effects of fibre orientation and front-surface reflection can be reduced if the sample is covered with a layer of powdered KBr. This approach was tried with the Narmco prepreg. In one case, the prepreg was covered with KBr which was then shaken off to leave a light sprinkling on the surface. In the second, a layer of KBr just sufficient to hide the surface was left in place. These two spectra are compared to the spectrum obtained without KBr in Figure 32. They are of rather poor quality because the overlayer of KBr reduces the spectral contrast considerably, especially when a thicker layer is used. The contrast is rather low to begin with, because of the graphite absorption.

Another approach was also tried. The prepreg was fully covered with powdered KBr, a piece of aluminium foil was placed on top, and the KBr was pressed into the resin using finger pressure. The sample was then inverted and tapped to shake off excess KBr, and the spectrum measured in the usual way. Although the resulting spectra are of lower contrast than those obtained without KBr, they are much more reproducible with respect to band shape, and the fibre orientation is found to have little or no effect on the quality, as shown in Figure 33. However, the band shapes are still somewhat different from those obtained in transmission. This suggests that front-surface reflection effects have not been eliminated, although they are more reproducible.

To check the effects of these treatments on the quantitative analysis, seven specimens from Batch 1014 were measured for each of the three conditions: no KBr, sprinkled with KBr, and KBr embedded. The spectra were treated as described above, using both Kubelka-Munk and absorbance units. Table 10 gives the results. Unfortunately, they show that sprinkling with KBr or embedding KBr in the prepreg do not improve the poor precision to any significant extent. Also, the ratios obtained with KBr present are substantially higher than those obtained without KBr, which are closer to those obtained in transmission. It appears that diffuse reflectance is of very limited use as a quantitative method for prepreg analysis, apparently because of front-surface reflection and scattering effects. Nevertheless, it can be of great value as a qualitative method for samples such as cured composites, which are difficult to measure by other means. In such cases it may also be of some use as a quantitative method if samples of significantly different composition are to be compared. Such is the case for the curing study described in the next section.

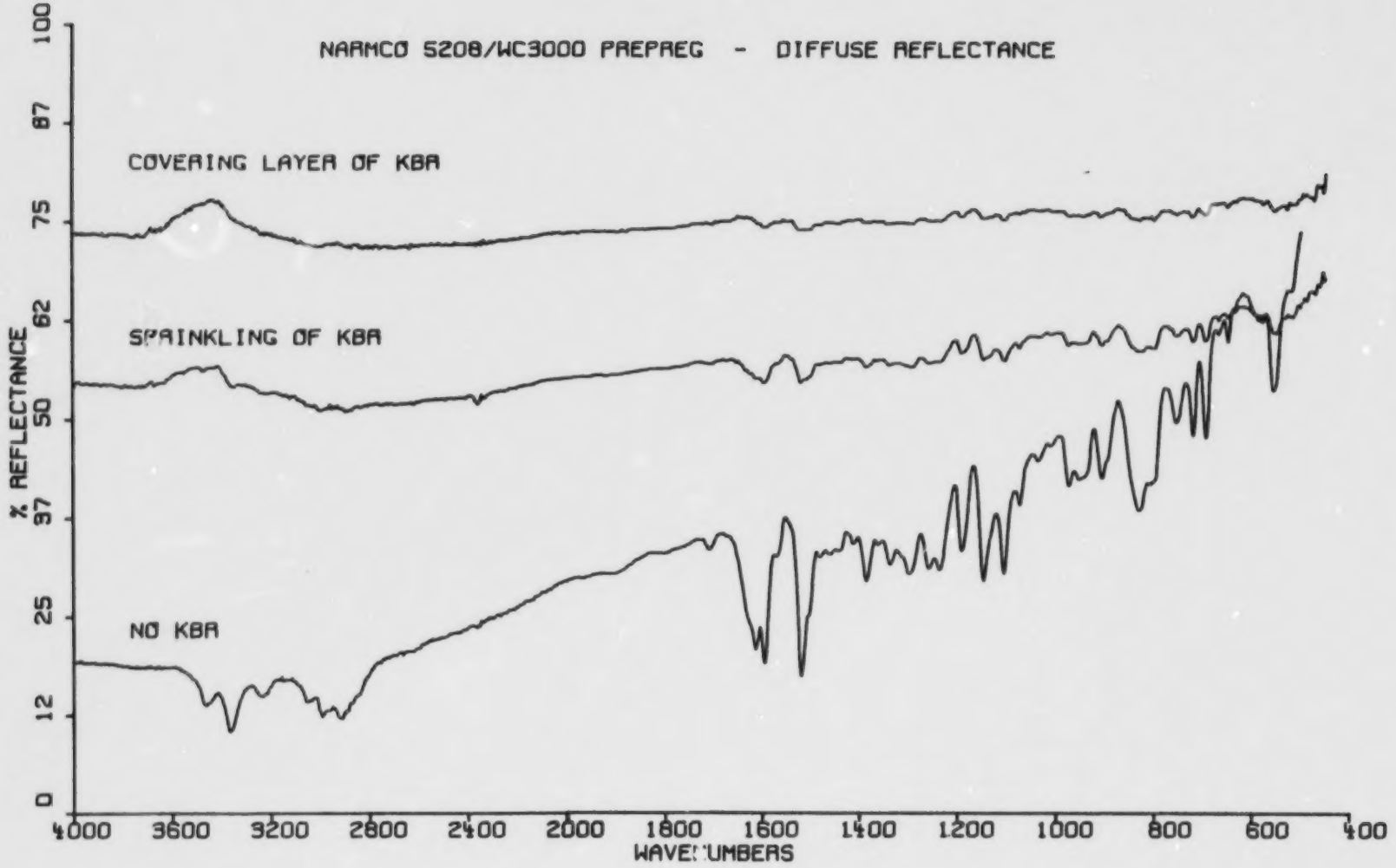


Figure 32 - Effect of covering with KBr on the diffuse reflectance IR spectrum of Narmco 5208/WC3000 prepreg.

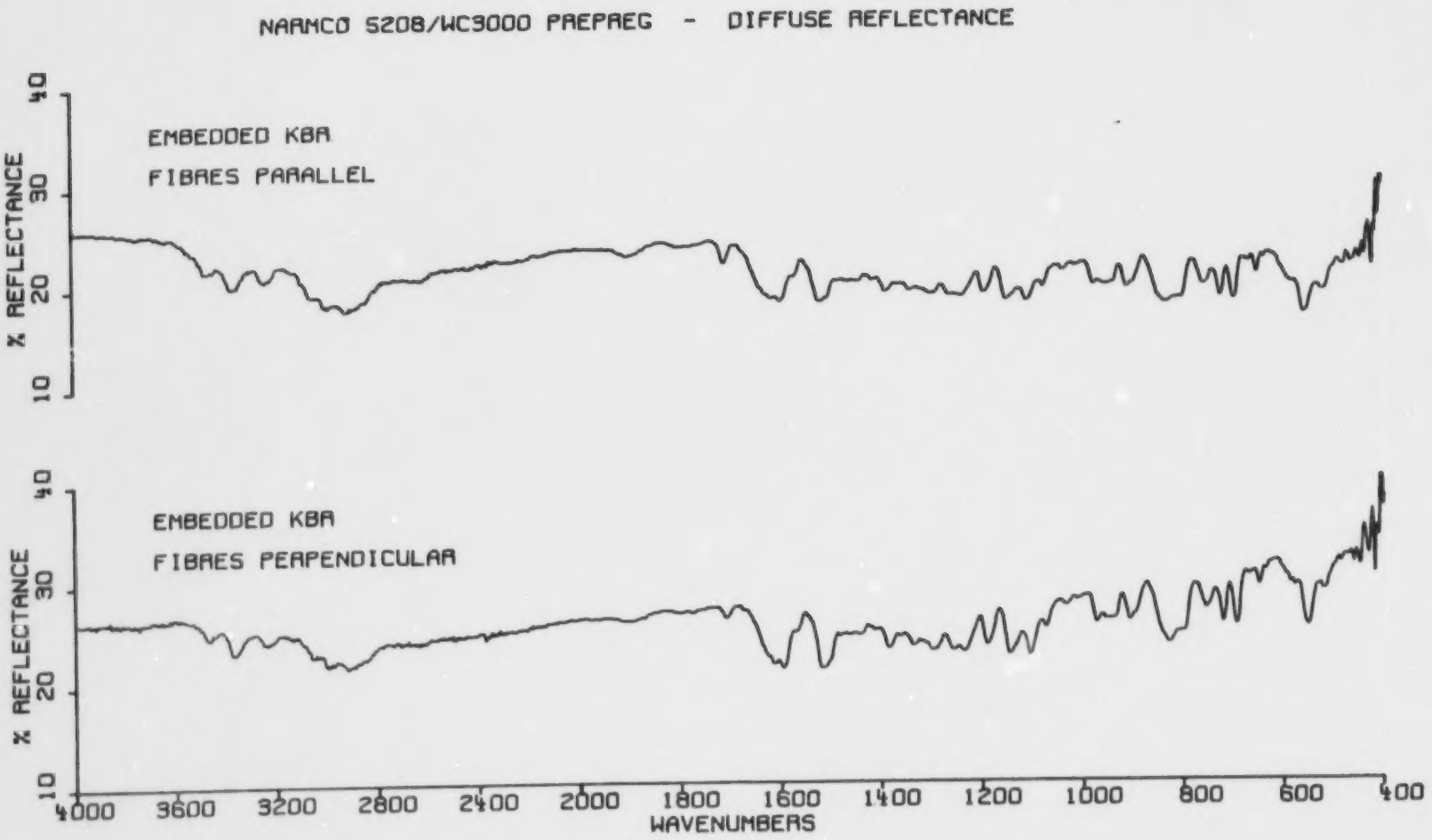


Figure 33 - Effect of embedded KBr on the diffuse reflectance IR spectrum of Narmco 5208/WC3000 prepreg.

Table 10. Quantitative analysis of Narmco 5208/WC3000 prepreg Batch 1014 by diffuse reflection IR

Conditions	Index = Band area divided by area of aromatic reference band			
	Single sulphone	Multiple sulphone	Single epoxy	Multiple epoxy
No KBr K-M units	0.323 (0.028, 8.6%)	0.855 (0.064, 7.4%)	0.167 (0.048, 28.9%)	0.541 (0.153, 28.1%)
No KBr Absorbance	0.438 (0.021, 4.7%)	1.272 (0.053, 4.1%)	0.314 (0.060, 19.2%)	1.005 (0.194, 19.3%)
KBr sprinkled K-M units	0.499 (0.045, 9.1%)	1.758 (0.084, 4.8%)	0.498 (0.134, 26.9%)	1.552 (0.397, 25.6%)
KBr sprinkled Absorbance	0.526 (0.064, 12.1%)	1.893 (0.135, 7.1%)	0.550 (0.118, 21.4%)	1.721 (0.345, 20.1%)
KBr embedded K-M units	0.501 (0.037, 7.5%)	1.863 (0.137, 7.4%)	0.483 (0.119, 24.7%)	1.484 (0.345, 23.2%)
KBr embedded Absorbance	0.508 (0.046, 9.1%)	1.934 (0.089, 4.6%)	0.527 (0.091, 17.2%)	1.622 (0.262, 16.2%)

5.5 Prepreg Cure

To demonstrate the usefulness of diffuse reflectance for studying actual composites, a study of the prepreg curing was performed using Batch 1014. A number of small squares of prepreg (about 1 cm x 1 cm) were cut and, after removal of the plastic backing sheet, were placed in sets of three between strips of Teflon-coated glass cloth. These were then put on a tray in an air-circulating oven, initially at room temperature. The oven was then turned on and set for 135°C. Two hours later the temperature was increased to 177°C and kept there for a further four hours. This cure programme is similar to the one used for

the IR transmission curing study described previously (Section 3.6), except that the heat-up rate is not controlled. At half-hour intervals, one set of three squares was quickly removed from the oven and cooled to room temperature. The three specimens were then measured in diffuse reflectance in the usual way. After conversion of the spectra to Kubelka-Munk units, followed by baseline correction, peak areas and ratios were calculated in the same way as in the transmission study. The limits of integration were adjusted as necessary to account for changes in the spectrum with cure. The evolution of the spectrum is illustrated in Figure 34, which may be directly compared with the transmission spectra of Figure 14; the similarities are obvious. The disappearance of the epoxy peaks at 1000-900 cm^{-1} is just as evident in the DR spectra as in transmission. Two features distinguish the DR spectra from the transmission ones. The first is the small acetone peak at 1708 cm^{-1} in the initial DR spectrum. The second is the appearance of carbonyl peaks at 1724 and 1668 cm^{-1} in the later DR spectra. These are due to oxidation and are not observed in the transmission study because curing was done inside the FTIR spectrometer, which is purged with dry nitrogen. The results of the peak area ratio calculations are shown in Figures 35 to 38. In the case of the epoxy indices, the curves have the same general shape as in the transmission study (Figures 17 and 18), but details are less apparent because of the high degree of scatter. In the case of the sulphone indices, there is an apparent gradual decrease over the period of the cure. In transmission, a decrease was observed for the single sulphone index but not for the multiple sulphone index. The reasons for this are not understood at present.

5.6 Microanalysis by Diffuse Reflection

Diffuse reflection is very useful for measuring the spectrum of a small quantity of sample. Two spectra are reported here to illustrate the high sensitivity.

The first (Figure 39) is that of pure TGDDM monomer, obtained by reverse-phase liquid chromatographic separation of MY 720 resin. A fraction of the eluting solution corresponding to the main peak of the chromatogram was collected at the detector outlet and the solvent (acetonitrile/water) was removed by passing a stream of nitrogen over the surface, followed by vacuum drying. The residue was dissolved in a few drops of acetone. A diffuse reflectance microsampling cup (3 mm diameter) from Harrick Scientific Corp. was filled with powdered KBr and the surface compacted and levelled with a spatula. The solution was deposited on the surface a drop or two at a time, allowing the solvent to evaporate after each addition. This was followed by vacuum drying for 15 to 30 minutes at room temperature to remove all the acetone. The spectrum was then recorded

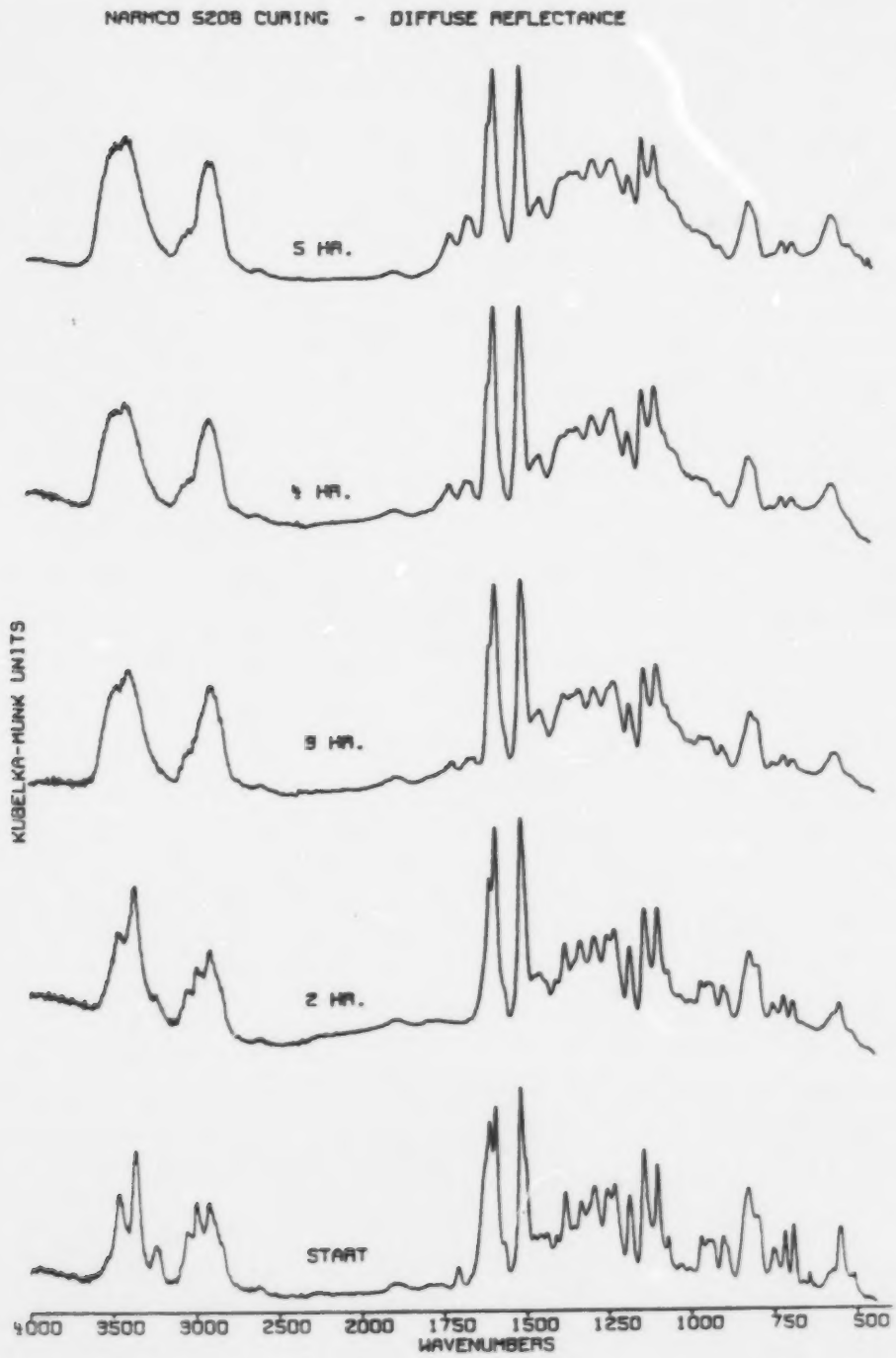


Figure 34 - Evolution of diffuse reflectance IR spectrum during cure of Narmco 5208/WC3000 prepreg.

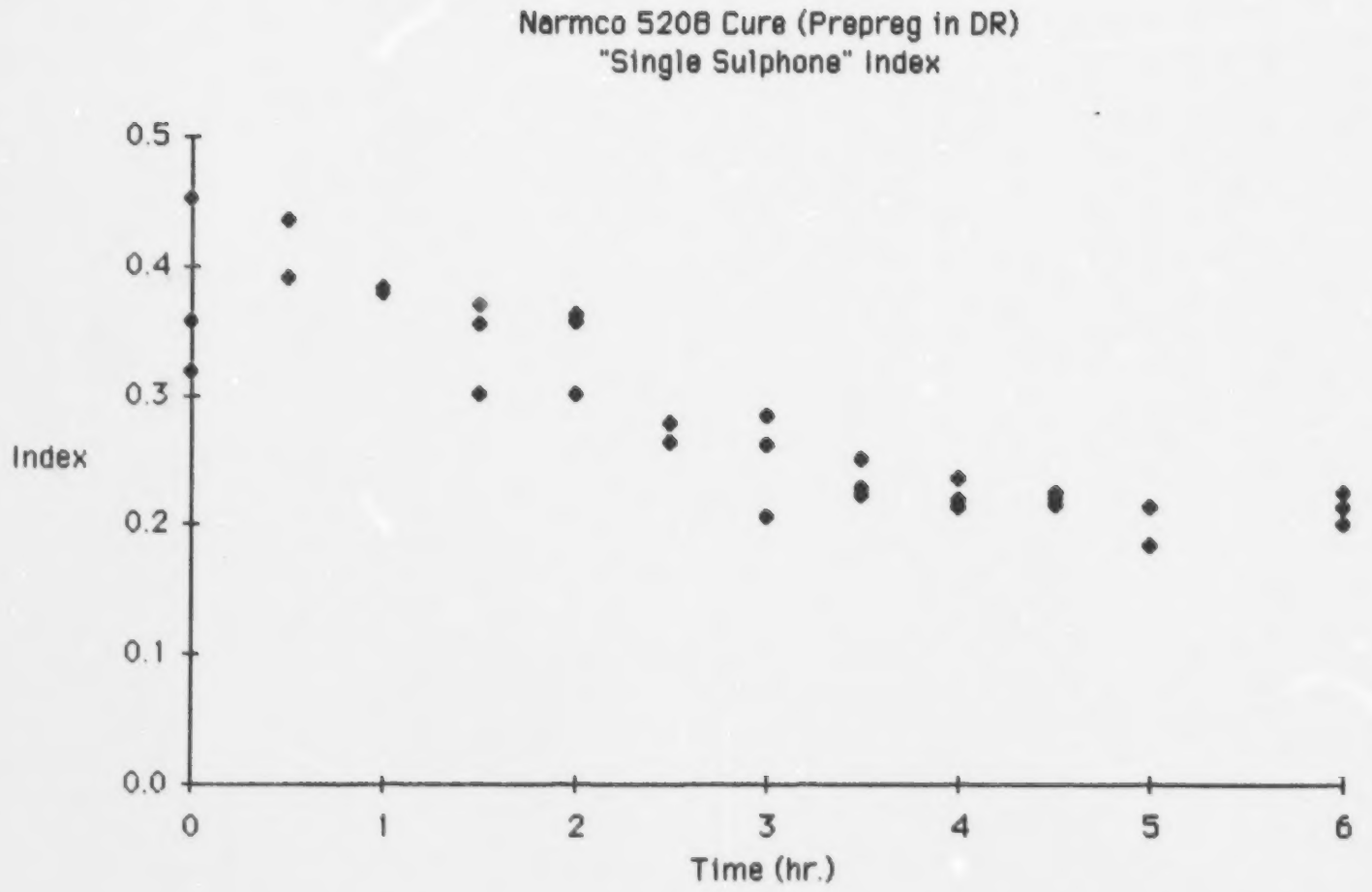


Figure 35 - Variation of "single sulphone" index as measured by diffuse reflectance IR during cure of Narmco 5208/WC3000 prepreg.

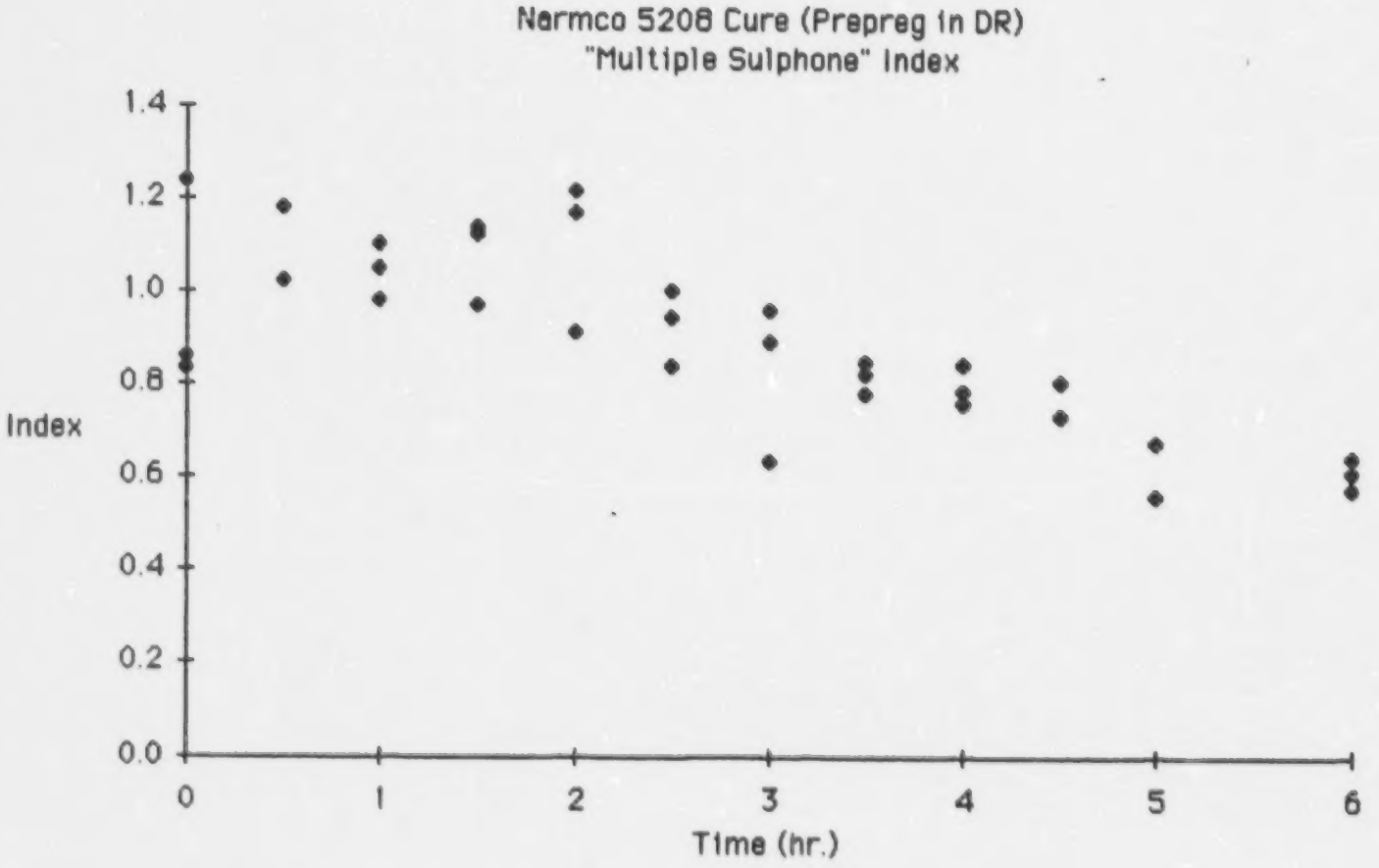


Figure 36 - Variation of "multiple sulphone" index as measured by diffuse reflectance IR during cure of Narmco 5208/WC3000 prepreg.

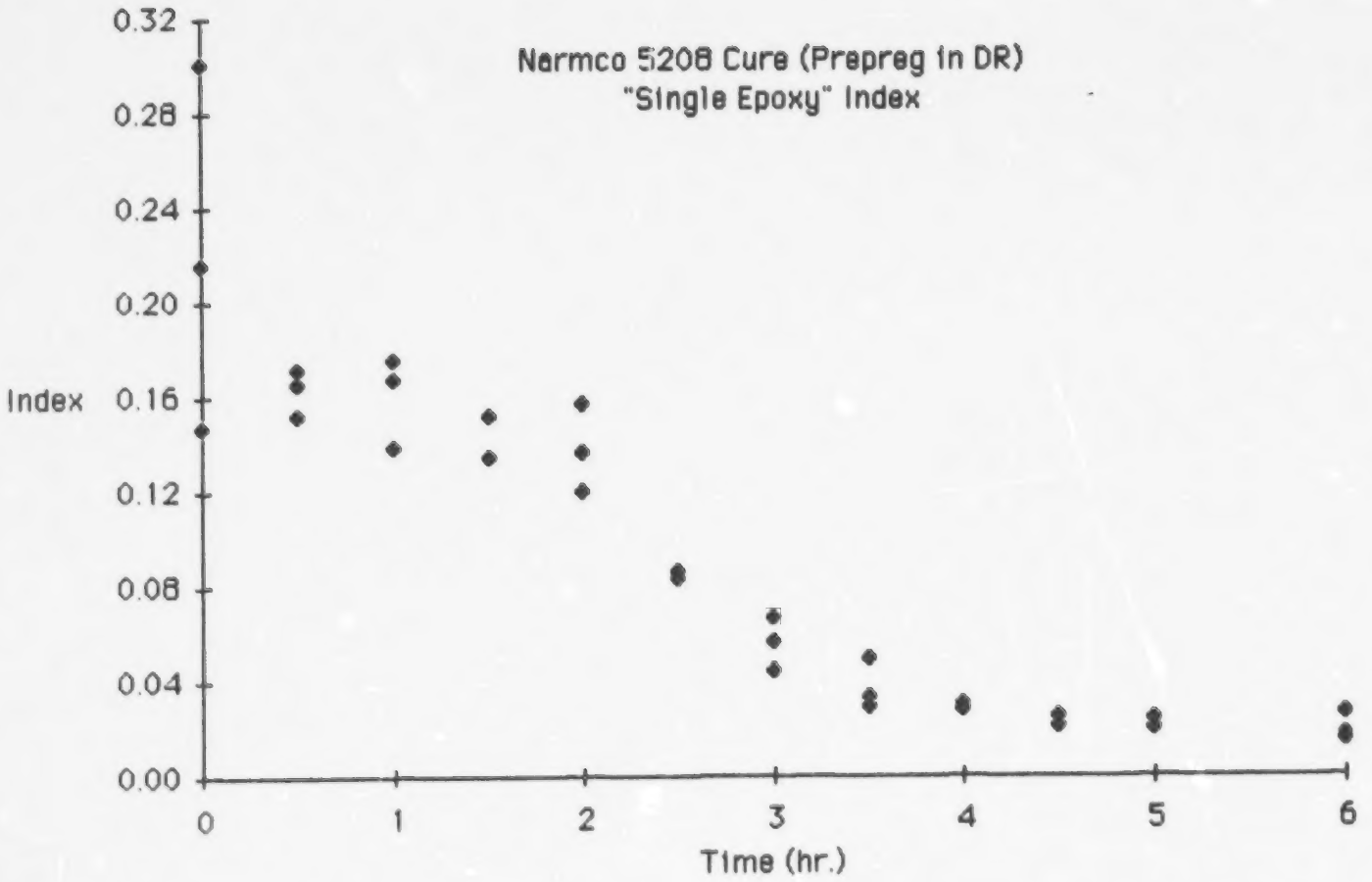


Figure 37 - Variation of "single epoxy" index as measured by diffuse reflectance IR during cure of Narmco 5208/WC3000 prepreg.

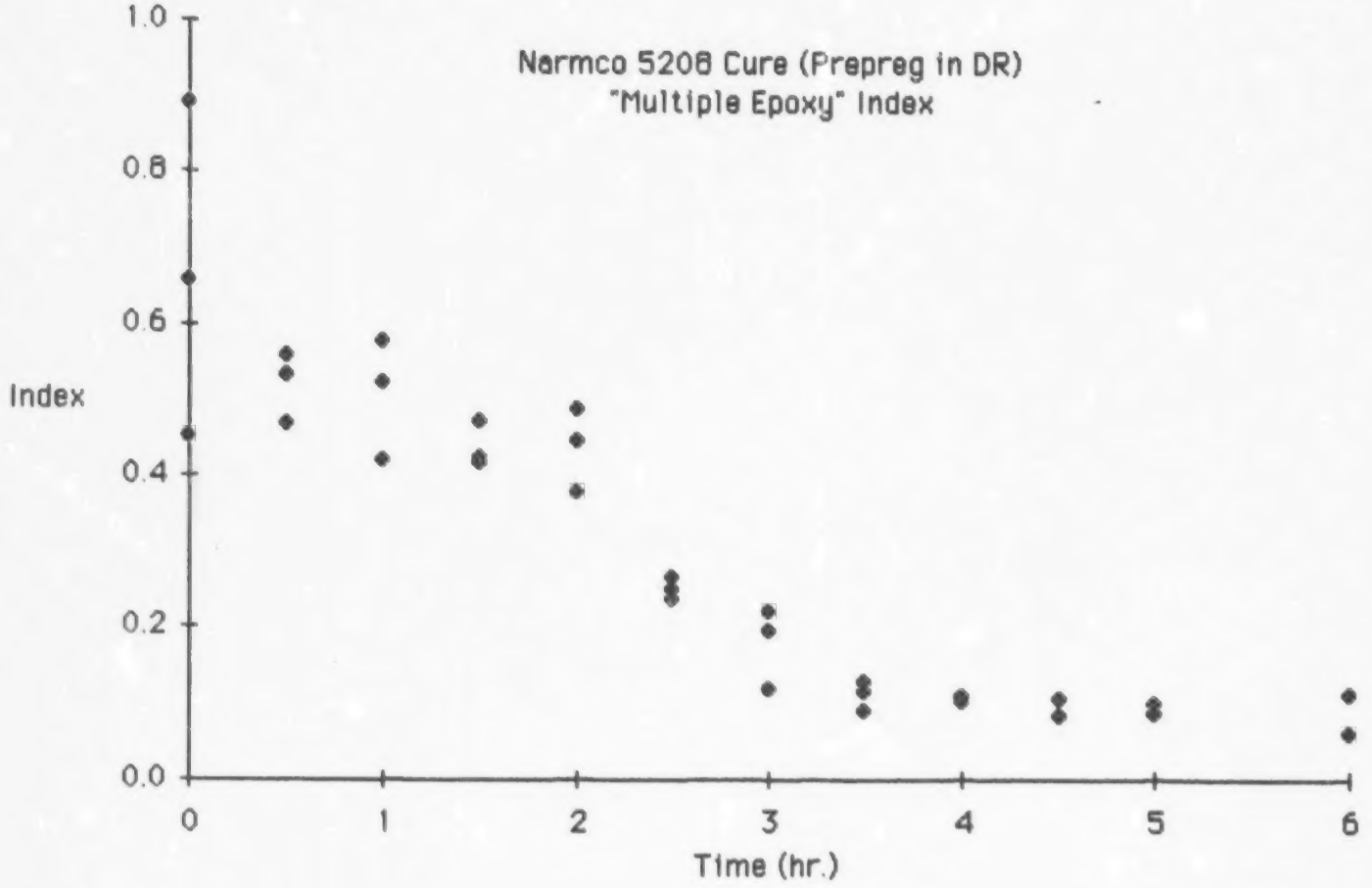


Figure 38 - Variation of "multiple epoxy" index as measured by diffuse reflectance IR during cure of Narmco 5208/WC3000 prepreg.

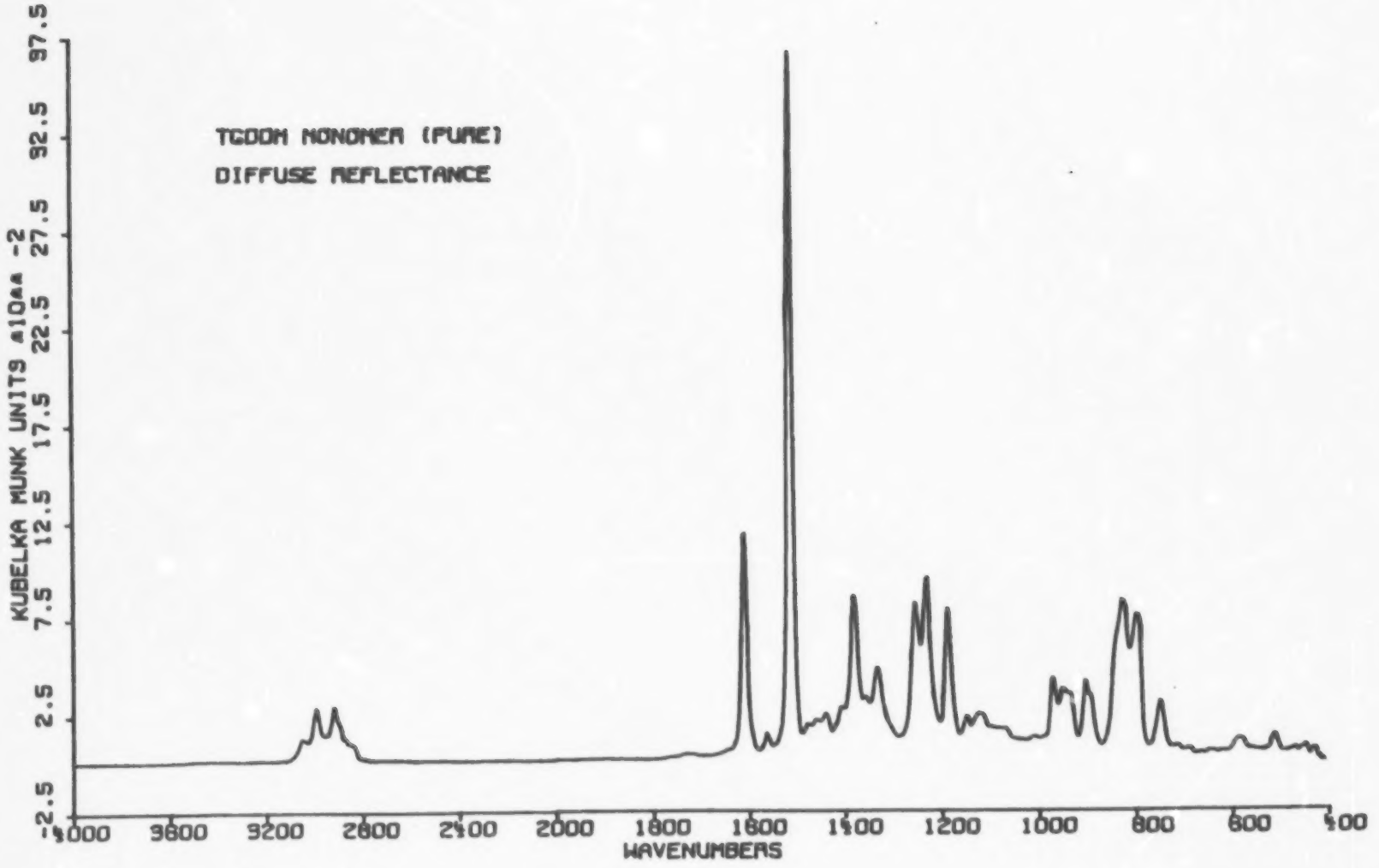


Figure 39 - Diffuse reflectance IR spectrum of pure TGDDM monomer obtained by liquid chromatographic separation of MY 720.

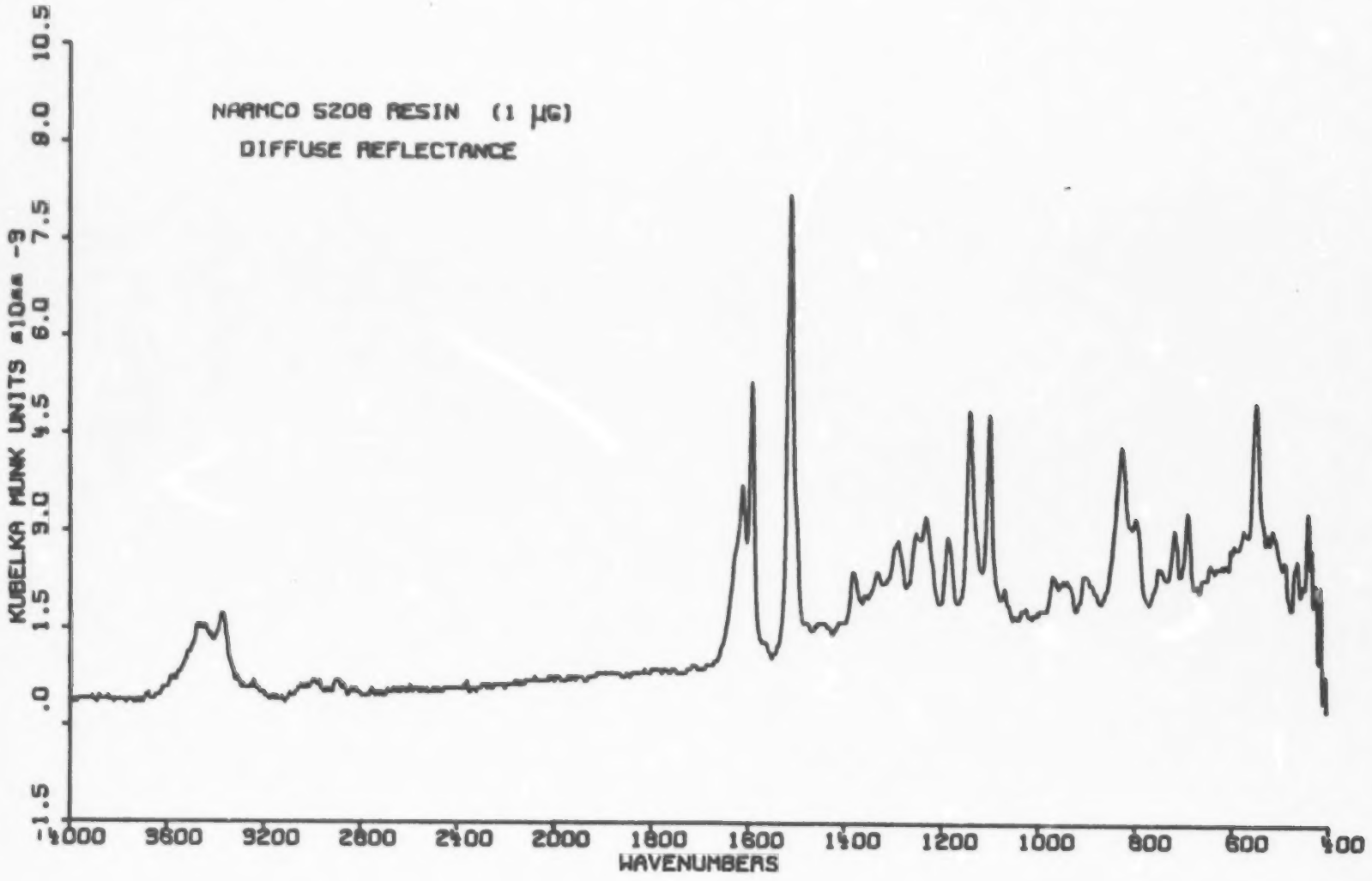


Figure 40 - Diffuse reflectance IR spectrum of 1 µg of Narmco 5208 resin.

using as a reference pure KBr. It closely resembles that of MY 720 (Figure 5), except for the absence of an OH band near 3500 cm^{-1}. This is because the monomer has no OH groups; they are present, however, in higher oligomers and in α-glycol by-products [51].

To check the sensitivity of the method, a solution of Narmco 5208 resin (Batch 1014) in acetone was prepared with a concentration of 0.1 g/L and a sample was prepared as described above using 10 μL of this solution. This corresponds to 1 μg of resin deposited on the KBr. The resulting spectrum (Figure 40) was measured using 512 scans. It is of good quality and is certainly sufficient to identify the resin.

5.7 Recommended Procedure for Measuring IR Spectra of Composites by Diffuse Reflection

(1) Make sure that the diffuse reflectance accessory is installed in the spectrometer and properly aligned.

(2) Prepare a potassium bromide reference sample by filling the appropriate sampling cup with ground KBr and compacting with a clean spatula to give a smooth surface.

(3) Prepreg and cured laminate samples are measured using a horizontal support of adjustable height, so that the sample surface can be adjusted to the same height as the potassium bromide reference sample. Preliminary trials should be done to find the optimum height adjustment (maximum energy throughput).

(4) Cut samples about 1 cm x 1 cm using scissors (for prepreg) or a jigsaw (for cured laminate).

(5) Affix the sample to the support. Prepreg is usually tacky enough to adhere by itself when pressed in place. This can be done with the fingers if the plastic backing sheet is left in place; the plastic is then carefully removed to record the spectrum of the freshly exposed surface. For cured samples, double-sided adhesive tape can be used. Avoid touching the surface to be measured with the fingers.

(6) If the fibre reinforcement does not have a plain weave pattern, the quality of the spectrum may depend on the orientation of the sample. In the Harrick "praying mantis"

accessory, best results are obtained if the principal fibre direction is parallel to the beam direction.

(7) Record spectra for both the KBr reference and the sample and take the ratio. It is recommended to accumulate at least 100 scans to obtain a good signal-to-noise ratio.

(8) If the spectrum is to be compared with transmission spectra, convert it to Kubelka-Munk units and do a baseline correction. This can then be compared to a transmission spectrum in absorbance units.

(9) Quantitative measurements are not recommended for diffuse reflectance spectra of this type of sample.

6. CONCLUSIONS

(1) Infrared spectroscopy, particularly Fourier transform infrared spectroscopy, is a very useful method for qualitative and quantitative analysis of high-performance composite systems. Spectra can be obtained by various methods (transmission, internal reflection, diffuse reflection), each of which has particular advantages and disadvantages.

(2) Quantitative analysis can be done based on the intensities of certain characteristic peaks in the spectrum. In the case of the Narmco 5208 epoxy resin system, these are the sulphone bands in the 1200-1100 cm^{-1} region arising from the DDS hardener and the bands at 1000-900 cm^{-1} arising from unreacted epoxide rings. The aromatic ring peak at 1517 cm^{-1} can be used as an internal reference. The peak at 830 cm^{-1} should not be used as a reference because it contains a shoulder at 800 cm^{-1} which is due to the epoxy groups. Better results are obtained if the sulphone and epoxy analysis is done using the area under multiple peaks rather than a single peak.

(3) The commonly used method for recording the spectrum, transmission through a thin film, requires separation of the resin from the fibre reinforcement. Sample preparation involves extraction of the resin from the prepreg with an organic solvent, followed by casting of a thin film on a transparent window. In quantitative analysis, substantial error can be produced if the film is not of uniform thickness. Good precision (a standard deviation of 2% or less) can only be achieved with very careful sample preparation. Acetone is recommended as solvent.

(4) The attenuated total reflection method can be used to obtain good spectra from uncured prepreg as is, thus avoiding solvent extraction and casting of a film. For quantitative analysis, the problem of nonuniform thickness associated with the transmission method does not exist, and good precision can be readily obtained (standard deviation under 2%). Better results are obtained using a germanium prism than with KRS-5. ATR is the recommended method for quantitative analysis of prepreg. It also allows detection of volatile components which are not detected by the transmission method.

(5) The diffuse reflection method also gives very good spectra and can be applied to both uncured prepreg and cured laminate. It is a rapid and "nondestructive" method. Although it gives excellent qualitative spectra, it is subject to effects arising from front-surface reflection and scattering which cause some variation in band shapes and

intensities. This severely limits its usefulness for quantitative analysis.

(6) The near-infrared region is also of interest for composite analysis. In the case of Narmco 5208, well-defined peaks appear in this region for unreacted epoxy groups and absorbed moisture.

(7) The curing of Narmco 5208 can be followed by infrared spectroscopy by means of the epoxy bands in the 1000-900 cm^{-1} region. Diffuse reflection can be used to confirm completion of cure in finished parts. It can also detect surface oxidation resulting in carbonyl peaks in the 1700 cm^{-1} region.

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